Macromol. Symp. ***174,*** *13–27 (2001)*

Rational Design of Polymer Colloids

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SUMMARY: Recent advances in understanding of the fundamental mechanistic events in emulsion polymerization give the potential for rational design of new materials based on polymer colloids. It is now possible to design a new industrial process from first principles, based on well-understood mechanistic principles. An overview of recent developments in the fundamental science of emulsion polymerization is given, with examples of the application of this knowledge to topologically-controlled synthesis of novel materials based on natural rubber and polybutadiene seed latexes.

Introduction

Emulsion polymerization is the basis for many industrial processes, and the production volume of modern latex technologies is continually expanding – a consequence of the many environmental, economic, and health and safety benefits the process has over solvent-based polymerization. A wide range of products are synthesized by emulsion polymerization, including commodity polymers such as neoprene (poly(chloroprene)), poly(tetrafluoroethylene) and SBR (styrene-butadiene rubber), paints, adhesives, paper coatings, and high-value added products such as supports for latex-based antibody diagnostic kits.

Emulsion polymerization has its roots in attempts to reproduce natural rubber latex, a material that was assuming great importance in the final years of the 19th century as applications of rubber multiplied in the industrialized world. In nations without ready access to tropical sources of natural rubber latex, there was a strong imperative to develop a synthetic substitute – the price of natural rubber peaked at US$2.88 a pound in 1910 1). It had been determined that natural rubber latex was a dispersion of polymer particles of the order of hundreds of nanometres to microns in water, stabilized by surface proteins and lipid surfactants, and that the repeating unit in natural rubber latex was equivalent to a polymer of isoprene (2-methyl butadiene). Accordingly, the first attempts to produce a rubber substitute involved dispersing isoprene in water using egg albumin, starch, or gelatin as a stabilizer 2). A similar procedure,

CCC 1022-1360/00/$ 17.50+.50/0

using a range of monomers and surfactants, was the basis for most synthetic rubber formulations over the next decades and eventually allowed the production of synthetic rubbers on a massive scale during the Second World War.

The original reasoning behind these formulations was that the emulsion droplets would be directly polymerized to give a dispersion of polymer particles of the same size. Advances were slow, and successful recipes were obtained by random variation of parameters, because the true mechanism of latex formation was far more complex.

As mechanistic knowledge emerged[3,4)], it became apparent that “emulsion polymerization” is in fact a misnomer: the emulsified droplets are not polymerized, and act solely as reservoirs for monomer while the polymer particles are formed by nucleation in the aqueous phase. This was not realized until the late 1940s, when Harkins set down the germ of the mechanism as it is understood today [3)]. Modern understanding (e.g. [5,6)]) shows that radicals are formed in the aqueous phase and add aqueous-phase monomer until they reach a chain length, z; where they become surface-active. At this chain length they can either enter a micelle (if surfactant is present above the critical micelle concentration: micellar nucleation), or enter a pre-existing particle, or propagate to a further critical chain length j_{crit} to collapse and swell with monomer to give homogeneous nucleation. Monomer continues to diffuse from monomer droplets to the new particles until the droplets are exhausted, and the final polymer particles are far smaller and more numerous than the original droplets.

The kinetics of emulsion polymerization are complex, involving a large number of species and at least two phases. The first quantitative approach to emulsion polymerization kinetics was by Smith and Ewart [7)], with later extensions by many others. The important events to consider are the free-radical reactions of chain formation: propagation, chain transfer, termination, and initiation; and the phase-transfer events that control particle formation: radical entry into particles from the aqueous phase, radical exit into the aqueous phase, radical entry into micelles, and the aqueous phase coil-globule transition.

This mechanistic knowledge has made the last 50 years of emulsion polymerization qualitatively different from the first 35. Use of seeded emulsion polymerization, in which a monomer-swollen polymer latex is used to absorb aqueous-phase radicals before they can generate new particles, allows separation of particle growth from particle formation and hence far more reproducible recipes. Means have been developed to separate the different kinetic events and study them independently, and this simplification has allowed continual incremental progress in the understanding of emulsion polymerization.

The rate coefficient for propagation (k_p), essential for quantitative interpretation of rate data, can be studied by pulsed initiation polymerization (PLP), a technique that has become well established only in the past decade (for a review, see 8)). Termination coefficients can be established by relaxation experiments performed with gamma-radiolysis initiated free-radical polymerization with large latex particles 9), while analysis of the molecular weight distribution under transfer-dominated conditions yield rate coefficients for chain transfer 10). Radical exit rate coefficients from small particles can be measured by gamma-radiolysis relaxation experiments 11,12), and in combination with the steady-state reaction rate and previously-measured exit rate coefficients can be used to determine the rate of radical entry 5).

PLP uses periodic flashes of laser light to generate bursts of radicals. At each burst, many chains are initiated, and many growing chains are terminated, by the large numbers of small free-radical species. If a sufficient number of chains are initiated and terminated by successive laser pulses, the point of inflection on the GPC (Gel Permeation Chromatography) trace of the polymer product will correspond to the molecular weight of these chains. This degree of polymerization L can then be expressed as

$$L = \frac{k_p[\mathrm{M}]}{\nu} \tag{1}$$

where [M] is the concentration of monomer, and ν is the frequency of the laser. The first suggestions for PLP appeared in 1977 13); the method was properly developed in the late 1980's 14) and its consistency proved and applied by an IUPAC working party 15-18), leading to its recommendation as the standard technique for measurement of k_p. It has now almost entirely superseded the rotating sector method. Internal consistency checks (varying laser frequency, wavelength, and power; measurement of first and second inflection points) make PLP a very robust and falsifiable experimental technique 19,20).

As reliable values of k_p are gradually collected, trends previously obscured in the scatter are becoming clear. For example, determination of the Arrhenius parameters for the broad range of acrylate 21-23) and methacrylate 24-31) monomers for which accurate data are now available has revealed that all acrylates have a large pre-exponential factor A and a low energy of activation E_A in propagation, while methacrylates have a low A and relatively high E_A. The explanation for this difference has been probed by accurate quantum chemical calculations of the transition state, and is related to subtle changes in delocalization in the transition state and other effects related to the methyl group [32).

A value of k_p enables the observed polymerization rate in an emulsion polymerization, R_p, to be related to a fundamental quantity in understanding kinetic processes in these heterogeneous systems, viz., the average number of radicals per polymer particle, $\bar{n}$, through:

$$R_p = k_p \bar{n} \left[\mathrm{M}_{\text{particle}}\right] \frac{N_c}{N_A} \tag{2}$$

where $[\mathrm{M}_{\text{particle}}]$ is the monomer concentration in the particle phase, N_c is the number of particles per litre of latex, and N_A is Avogadro's constant. Further mechanistic inferences given below use eq 2, with seeded studies wherein secondary particle formation is avoided (and thus N_c is known), $[\mathrm{M}_{\text{particle}}]$ is specified by controlling the initial amount of added monomer used to swell the seed, and k_p is known from PLP systems; the time evolution and steady-state value of $\bar{n}$ can thus be found from experimental observations of the time evolution and steady-state value of R_p.

Termination rate coefficients can be measured using the γ-radiolysis relaxation method. This involves initiation using γ radiation, followed by removal of the reaction vessel from the γ source. Conversion during the relaxation period is monitored by dilatometry, and the decay in polymerization rate over time can be easily related to the rate of radical loss 33). When large particles are used, radical loss will be dominated by intra-particle termination, rather than exit into the aqueous phase, and the rate coefficient for termination can be determined from the decay curve. By using multiple insertions and removal, the termination rate coefficient can be determined over a wide range of polymer weight fraction (w_p).

A reliable theory for termination applicable to the range of w_p in emulsion polymerizations has now emerged. The combination of two radical species, the most common form of termination reaction, should have no activation barrier. Hence in a condensed phase the reaction will be purely diffusion-controlled. The termination rate coefficient, k_t, will therefore have separate values for each combination of radical chains of different lengths. These coefficients, k_t^{ij}, may be estimated by the expression 34,35)

$$k_t^{ij} = 2\pi p_{ij}(D_i+D_j)\, \mathrm{r}\, N_A \tag{3}$$

where D_i and D_j are the diffusion coefficients of polymer radicals of degrees of polymerization i and j, respectively, r is the sum of the van der Waals radii of the monomer, and p_{ij} is the probability that the two spins will be anti-parallel and therefore able to form a bond (this varies from ¼ under conditions of rapid diffusion to 1 under slow diffusive conditions where spin inversion is possible). From pulse field gradient NMR spectroscopy of oligomer diffusion in polymer matrices, a scaling relationship has been obtained which has been found to hold for oligomers based on a range of monomers (styrene, methyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate) 36,37). This relates the diffusion coefficient of a monomer at a particular weight fraction, $D_{\text{monomer}}(w_{\text{p}})$, to that of the corresponding oligomers at the same weight fraction:

$$D_j\left(w_p\right) = \frac{D_{\text{monomer}}\left(w_p\right)}{j^{0.66 + 2.0\text{w}_\text{p}}} \tag{4}$$

Combining expressions (3) and (4) shows that termination is dominated by "short-long" termination: most termination is by very short, mobile radicals reacting with large polymer radicals that are essentially trapped in the matrix, even when this monomer/polymer matrix is rubbery. The observable termination rate coefficient, $<k_{\text{t}}>$, is an average of k_{t}^{ij} over the distribution of radicals of varying degrees of polymerization. Experimentally, rate coefficients have been measured that are in acceptable agreement with this diffusion-controlled model 38).

Exit of radicals from the polymer particles to the aqueous phase can also be investigated using γ-radiolysis relaxation experiments. Instead of using large particles where radical loss is dominated by termination, small particles where exit dominates the relaxation behavior are used. Under most conditions, the fate of exited radicals is to enter other polymer particles and remain therein, when the rate of radical loss per particle is given by

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho_{\text{thermal}}\left(1 - 2\bar{n}\right) - 2k\bar{n}^2 \tag{5}$$

where k is the exit rate coefficient, and ρ_{thermal} is that of spontaneous generation of radical species. The mechanism of exit is believed to be chain transfer to monomer, followed by competition between propagation to form a species trapped within the polymer particle and diffusion away from the surface of the particle. From this can be derived the expression 39,40)

$$k = \frac{3D_\mathrm{w}\left[\mathrm{M}_\mathrm{water}\right]k_\mathrm{tr}}{k_\mathrm{p}^1\left[\mathrm{M}_\mathrm{particle}\right]\left(r_s\right)^2} \tag{6}$$

where D_W is the diffusion coefficient of monomer in water, $[\mathrm{M_{water}}]$ is the monomer concentration in the water phase, k_tr is the rate coefficient for transfer to monomer, $k_\mathrm{p}{}^1$ is that for propagation of a monomeric radical, and r_S is the swollen radius of monomer. Figure 1 (re-processing data from [12]) shows that eq 6 provides excellent agreement with experimental data [12].

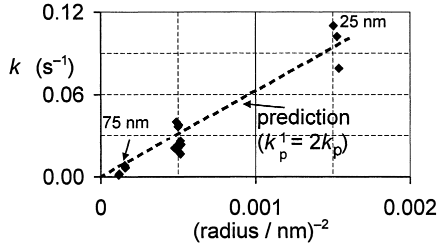

Fig. 1: Exit rate coefficients determined by γ-radiolysis relaxation as a function of unswollen particle radius, as determined from experiment and as calculated from eq 5.

Entry coefficients can be determined by measuring the steady-state rate in a chemically initiated system, and hence (from eq 2) the steady-state value for $\bar{n}$ with a chemical initiator. Taking the exit rate coefficient determined by γ-radiolysis relaxation, it is then possible to determine the entry rate coefficient ρ using eq 5. Data for most systems indicate relatively low initiator efficiency, which can be attributed to termination of growing radicals in the aqueous phase before entry. The model developed by Maxwell *et al.*[41] is that entry occurs only when aqueous-phase propagation yields an oligomer of degree of polymerization z (which, for persulfate initiator, would have the composition $\bullet\mathrm{M_zSO_4^-}$). This mechanism yields, under certain approximations, the following result:

$$\rho = \frac{2k_\mathrm{d}[\mathrm{I}]\,N_A}{N_c}\left[\frac{2\sqrt{k_\mathrm{d}[\mathrm{I}]k_\mathrm{t,water}}}{k_\mathrm{p,water}[\mathrm{M}]_\mathrm{water}} + 1\right]^{1-z} \tag{7}$$

where k_d is the rate coefficient for dissociation of initiator, [I] is the initiator concentration, and $k_\mathrm{p,water}$ and $k_\mathrm{t,water}$ are respectively the propagation and termination rate coefficients in the aqueous phase. Figure 2 (re-plotted from data in [42]) illustrates (as has been shown previously for many other systems [5]) that this mechanism gives a good fit to experimentally determined values of ρ for styrene particles stabilized both by anionic surfactant and by a small amount of electrosteric stabilizer, although the model does *not* fit for such particles with a thick coating of electrosteric stabilizer [42)].

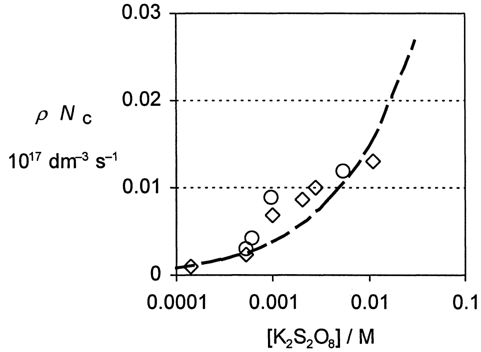

Fig. 2: entry rate coefficient ρ (plotted as ρN_c, as suggested by eq 7) for seeded emulsion polymerization of styrene at 50°C with persulfate initiator, ~ 40 nm unswollen seed radius stabilized by SDS (E) and by a light coverage of electrosteric stabilizer made by adding styrene and acrylic acid to the seed and polymerizing to 5% conversion (A); points, experimental, line, prediction of eq 7.

Reliable methods of determining rate coefficients for chain transfer have been developed, based on the relative simplicity of the chain length distribution formed under conditions where termination is dominated by chain transfer [10,43,44)]. As yet, there has been no systematic collection of data in order to deduce trends in Arrhenius parameters, as has begun to be profitable with k_p values. Quantum calculations on chain transfer reactions are also in a very preliminary stage [45)].

The mechanisms and rate coefficients obtained as described can be used in an extensive *a priori* model for particle formation in emulsion polymerization [46)]. The conditions under which the polymerization is carried out will determine which nucleation mechanism will predominate; above the CMC, micellar nucleation is expected, while below the CMC homogeneous nucleation will dominate under conditions where no seed is present. This model has been used to simulate sensitive data on particle formation, a highly variable process that could be considered the 'last frontier' of modelling emulsion homopolymerization. In systems such as styrene, MMA and butyl acrylate, where all rate parameters required in the model can be obtained by independent measurements (PLP, seeded experiments), it has proved possible to predict particle number (and hence size) with quite acceptable reliability.

Using Mechanistic Knowledge to Design New Materials

Understanding the fundamental mechanisms of emulsion polymerization has now advanced to such a stage that intelligent design of materials enables novel products with desired end-use properties to be produced with a fraction of the time and effort involved in traditional development methods (i.e., incremental variation of existing system parameters). Two classes of material of interest are

- Graft copolymers between hydrophobic and hydrophilic monomers, taking advantage of the separate phases present in a latex. These modified latexes have novel colloidal and compatibilizing properties.
- Controlled grafting of immiscible polymers to form new single-phase blends with novel mechanical properties; e.g, a homogenous graft polymer of poly(isoprene) and poly(MMA) showing novel mechanical properties.

One substrate with excellent potential for both of these grafting reactions is natural rubber latex. The original inspiration for emulsion polymerization is still of commercial importance, due to the very high degree of stereoregularity (close to 100% *cis*-poly(isoprene)) achieved by biosynthesis. This stereoregular polymer forms films with exceptional barrier properties (e.g., to prevent the passage of viruses) that actually become stronger upon stretching. These properties are vital for the major uses of natural rubber in surgical gloves and condoms, and cannot be economically duplicated synthetically.

Problems with natural rubber latex are its extreme polydispersity and high content of proteins, phospholipids, and inorganic salts. All of these factors complicate its processability, and allergic sensitivity to the protein components of natural rubber has become major concern. The mechanistic understanding now available provides the opportunity to overcome these problems and to create improved materials using natural rubber latex as a substrate. Besides its mechanical properties, natural rubber latex is important as a renewable resource – expanding its range of applications to fields currently dominated by purely synthetic polymers has obvious benefits for tropical nations dependent on imported oil.

Topology-Controlled Emulsion Polymerization

In order to graft a hydrophilic monomer to a hydrophobic substrate, it is desirable to generate radicals at the interface between the aqueous and organic phases of a latex. This can be achieved by using a two-part redox initiation system, in which one half of the couple is a water-soluble species predominantly existing in the aqueous phase and the other is partitioned primarily into the organic phase [47)]. Under these conditions, radicals will be generated at the one location in the system where the two species can meet: at the interface. This reaction has been carried out in our laboratories with poly(butadiene), poly(isoprene) and poly(styrene) latex substrates, with excellent results in all three cases. Typical conditions use cumene hydroperoxide as the organic-phase half of the couple and tetraethylene pentamine (with a trace of Fe^{2+}) in the aqueous phase, with potassium oleate as surfactant and gentle reaction temperatures between 10 and 50°C.

Grafting sites can only be generated by abstraction from poly(styrene), which has a relatively labile methine hydrogen site on the backbone. In the case of the polydiene substrates, however, both abstraction of an allylic hydrogen or addition across the double bond of the backbone are possible ways to generate grafting sites. Use of the relatively bulky cumyloxy radical in the organic phase will favour abstraction over addition, and the absence of addition reactions to the model compound squalene (a C_{30} analog of poly(isoprene)) has been verified by nitroxide spin-trapping [47)].

Dimethylaminoethyl methacrylate (DMAEMA), a water-soluble monomer, was used to generate the hydrophilic grafted chains. In order to prove that grafting of this polymer to the latex had occurred, latexes were subjected to double Soxhlet extraction with toluene and with water to remove the fractions soluble in each solvent. The residual insoluble portion was then characterized by solid-state ^{13}C-NMR spectroscopy. The assumption is made that any poly-(DMAEMA) present in the insoluble fraction after the double extraction is grafted to the substrate. A representative result for cross-polarization experiments performed on the insoluble fraction of modified poly(butadiene) is shown in Figure 3.

The grafted latices prepared by this method show greatly enhanced colloidal stability, strong evidence for the existence of an electrosterically-stabilizing poly(DMAEMA) layer on the particle surfaces. For example, while natural rubber latex (NRL) is very *p*H sensitive and will coagulate below a pH of approximately 9, the modified NRL was indefinitely stable at *p*H 2.0. This finding is of possible practical importance, as it may help find a solution to one of the most pressing problems facing the NRL industry: the allergic reactions to natural rubber proteins that make latex gloves unusable for as many as 10% of medical professionals.

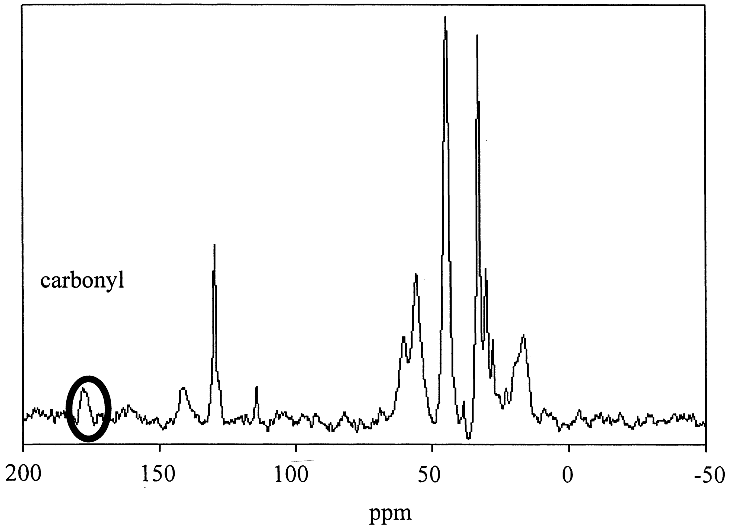

Fig. 3: CP-MAS ^{13}C-NMR spectrum of DMAEMA-grafted poly(butadiene).

Achieving Homogeneous Blended Latices

Most blends of two polymers will separate into discrete phases; the Flory-Huggins equation predicts that except in the few cases where there is a coincidental similarity of solubility parameters, different polymers will be immiscible. For example, when natural rubber latex is swollen with MMA and this monomer polymerized *in-situ* in a seeded emulsion polymerization, the polymer particles that are formed display distinctive 'fruitcake' morphology (small inclusions of pMMA in a natural rubber matrix) 48-50).

Two reasons are suspected to contribute to the inhomogeneity seen in these particles 49):

- Poor grafting of poly(MMA) to the substrate, and thus a low amount of *in-situ* compatibilizer.
- Formation of secondary particles and their imbibement by the NRL particles

The protein stabilizer around the outside of the polymer particles in NRL may inhibit entry , enhancing the possibility that nucleation will take place in the aqueous phase, leading to the formation of poly(MMA) particles which can subsequently be imbibed. One way to avoid this problem is to employ a system where the number of aqueous-phase radicals is minimized; i..e., employ a monomer that is highly insoluble in water. This should greatly reduce secondary nucleation.

In order to enhance grafting, it is desirable to have a monomer which is reactive enough to propagate with the stable allylic radical formed by hydrogen abstraction from the poly(isoprene) backbone. Acrylates are much more reactive monomers than methacrylates, for example as seen in their k_p from PLP.

Dodecyl acrylate (DA) is an ideal monomer satisfying both criteria for maximizing homogeneity: it is both highly reactive and has very low water solubility. Polymerization of DA in natural rubber latex gives the expected result, particles with a uniform morphology. This homogeneous blend of DA and natural rubber is a novel material 49). When dodecyl methacrylate (DMA) is used, separate poly(DMA) domains can clearly be seen. This is attributed to reduced grafting, due to the lesser reactivity of the methacrylate species in comparison to the acrylate 51).

Addition of vinyl neo-decanoate (VneoD), another monomer with low water solubility, can also enhance the degree of grafting in MMA A relatively unreactive monomer, VneoD will not add to an allylic radical, but it forms a highly reactive radical which can readily abstract from poly(isoprene) to form additional grafting sites. When a 9:1 feed of MMA:VneoD is used, homogeneous particles of modified NRL can be formed. Dynamic mechanical analysis is a powerful tool in judging the homogeneity and mechanical properties of these MMA-NRL graft materials. The temperature dependence of tanδ for these latexes compared to that of corresponding blends gives a clear indication of extensive grafting. The frequency dependences of the storage and loss moduli (Figure 4) suggest novel mechanical properties of possible application in pressure-sensitive adhesives 52).

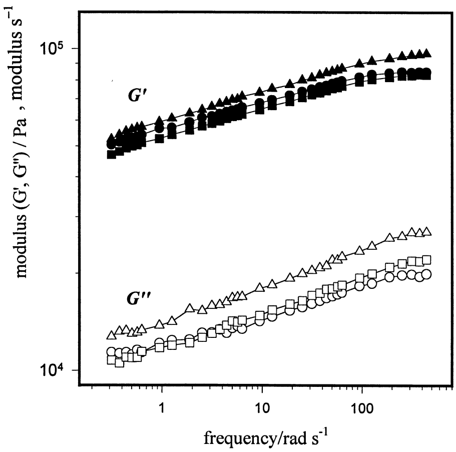

Fig. 4: Storage and loss moduli as functions of frequency at 25 °C for modified natural rubber latexes. ○: NR-g-PMMA, □: NR-g-PMMA/VneoD10%, and △: NR-g-PMMA/VneoD20%.

Conclusions

Emulsion polymerization can be used to achieve *topological control* in free-radical polymerization. Knowledge of the mechanisms of free-radical and colloidal growth indicates appropriate synthetic procedures which can be used to produce valuable new materials. Almost a hundred years ago, emulsion polymerization began as an effort to imitate natural rubber; today, the same techniques can be used to take natural rubber latex and improve it. The challenge that faced emulsion polymerization throughout the 20th century was to design a new industrial process on mechanistic principles: to choose desired customer properties, such as reduced water sensitivity, or particular rheological properties, and design a system that will give these properties. The rapid advances in the mechanistic understanding of emulsion polymerization over the last decade mean that we now have the capacity to meet this challenge.

Acknowledgements

The authors are glad to acknowledge the support of the Australian Research Council for an International Research Exchange Fellowship (D-YL), of Elf Atochem, BASF and the Dow Chemical Corporation. We greatly appreciate the assistance of Andrew Whittaker of the University of Queensland. The Key Centre for Polymer Colloids is established and supported under the Australian Research Council's Research Centres Program.

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