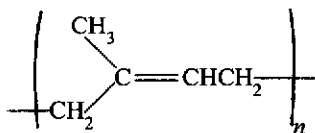


## Use of Mechanistic Principles to Make Modified Natural Rubber Latex Products by Emulsion Polymerisation<sup>†</sup>

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*A novel class of materials, comprising an artificial polymer inside natural rubber latex particles, so that the new polymer is extensively grafted to the cis-polyisoprene, can be made if the artificial polymer is of very low water solubility, with the natural rubber latex (NRL) used as seed. This avoids the problem of secondary particle formation and subsequent engulfing of the resulting precursor particle into the pre-existing latex particles, which gives inhomogeneities in the conventional means of making modified NRL through such seed technology.*

Commercial high-ammonia natural rubber latex (NRL) comprises almost entirely of *cis*-polyisoprene:



stabilised by adsorbed long-chain fatty-acid soap which are hydrolysis products of phospholipids; polypeptides from hydrolysis of the original proteins are also adsorbed on the surface<sup>1</sup>. NRL is highly polydisperse in regards to its particle size distribution.

Natural rubber has many advantages for certain applications. An extension of the properties of natural rubber latex would be possible if one could graft a second polymer within a natural rubber latex particle, using the well-established technique of emulsion polymerisation of artificial polymers<sup>2</sup>. Such a novel material could lead to many technical applications, depending for example on the glass transition temperature of the second polymer. Included in the potential advantages of such a process is that natural rubber is a renewable resource.

The reason that one might suppose that extensive grafting of a second polymer would

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be possible is as follows. Normally, second-stage growth would result in separation of the two phases, because of the incompatibility of any two different polymers (above a minimal molecular weight). However, given reasonable reactivity ratios, one might expect that sufficient grafting of the second polymer into the double bond on the *cis*-polyisoprene, this would result in the formation of *in situ* compatibiliser which should prevent the separation of the *cis*-polyisoprene and the new polymer. However, as is well known, if one attempts to perform such a growth using conventional seeded technology, the resulting product is highly heterogeneous (see, for example Reference 3); effectively, a 'fruit-cake' morphology results. This heterogeneity is evidenced both by the morphology as seen in electron microscopy studies and also in  $T_g$  data, where it is seen that the glass transition temperature of the product of such a polymerisation has a peak corresponding exactly to that of natural rubber.

We postulate here that an origin for the heterogeneity observed when NRL is used as a seed is that *secondary particle formation* occurs easily (for reasons discussed in the next section); the new particles so formed tend to be subsequently engulfed by the soft NRL particles (*Figure 1*). These domains are then rich in the second polymer, and so become the principal locus for subsequent polymerisation, resulting in heterogeneity.

#### MECHANISMS OF PARTICLE FORMATION AND RADICAL ENTRY

The mechanisms for particle formation and of entry of radicals into pre-existing particles in an emulsion polymerisation are well established<sup>2</sup>. These mechanisms are illustrated in *Figure 2*, for a system where the concentration of surfactant is below the cmc,

with persulphate initiator. The most important parts of the mechanism for the present purposes comprise the *competition between entry and particle formation*: an aqueous-phase radical formed from initiator can grow to a critical degree of polymerisation  $z$ , when it becomes surface-active and may enter a pre-existing particle<sup>4</sup>, or may grow further until it reaches another critical degree of polymerisation  $J_{crit}$ , when it collapses to form a new particle by homogeneous nucleation<sup>5</sup>.

It is thus apparent that avoidance of secondary particle formation involves this fundamental criterion of the competition between entry and particle formation<sup>6</sup>. There are several means of doing this (e.g., controlling the initiator type or number density of pre-existing, or seed, particles), since to some extent one may control each of the various mechanisms in *Figure 2* separately.

Over the years, techniques have been developed<sup>2</sup> for obtaining unambiguous values for entry rate coefficients in emulsion polymerisation systems. The optimal method for this involves using growth in a seeded system, in the absence of secondary particle formation, and choosing conditions so that particle growth is controlled by 'zero-one' kinetics, entry of a radical into a particle which already contains a growing radical results in instantaneous termination, so that particle growth involves only propagation, entry and exit (desorption). The kinetics of radical loss are then obtained by initiating with  $\gamma$  radiolysis and then removing from the  $\gamma$  source, which yields the exit rate coefficient. The steady-state rate with a chemical initiator is then measured, from which a knowledge of the exit rate coefficient then yields that for which radicals from the chemical initiator enter the particles.

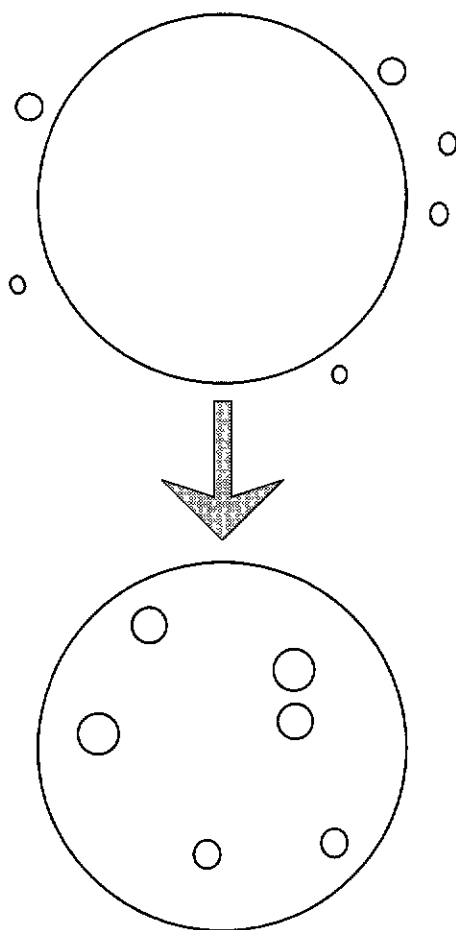


Figure 1. How secondary nucleation followed by engulfment can lead to a "fruit-cake" morphology.

What is especially important for controlling secondary particle formation in NRL is that such studies have shown that the presence of any polymeric layer around the particles has a dramatic effect on the kinetics: *inter alia*, the rate coefficient for entry is greatly reduced<sup>7</sup>. It has been postulated that this reduction is because the 'hairy layer' of polymer surrounding the particle slows down the rate at

which a z-mer diffuses through the interfacial regime. For systems stabilised by *anionic* surfactant, there is considerable evidence<sup>4,7,8</sup> that the diffusion of a z-mer through the interfacial layer which is one of the mechanisms for particle entry shown in Figure 2 is not rate-determining, whereas this step probably is rate-determining for systems containing *polymeric* stabiliser (or, in the case of NRL,

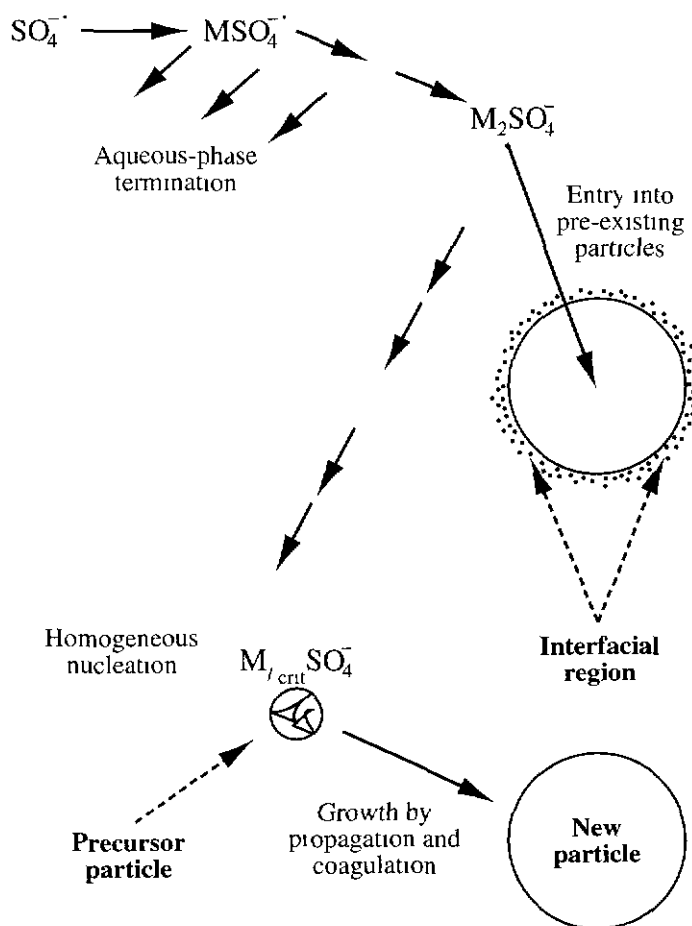


Figure 2 Particle formation and growth in an emulsion polymerisation below the cmc

where there is adsorbed hydrolysed protein around the particles).

This reduction in the entry rate coefficient for a system such as NRL, together with our postulate that inhomogeneity derives at least in part from particles formed by secondary nucleation being subsequently engulfed within

NRL particles, explains why it seems so difficult to have extensive grafting in a NRL: the reduction in the entry rate coefficient implies that radicals which otherwise would have entered tend instead to form new particles, which are subsequently engulfed and form domains.

## STRATEGY FOR AVOIDING SECONDARY PARTICLE FORMATION IN NRL

The forgoing postulate suggests that extensive grafting in NRL requires avoiding secondary particle formation. One way might be to try an initiator such as AIBN, which being hydrophobic will form radicals within the particles. However, this initiator is sufficiently soluble in the aqueous phase that some radicals can form in the aqueous phase as well as within the particles, and so this will not avoid secondary nucleation. Instead, a suitable strategy to avoid secondary particle formation and thus bring about extensive grafting<sup>9</sup> would be to use a system where formation of  $j_{\text{crit}}$ -mers is impossible. This can be effected by carrying out the polymerisation with a monomer that is *highly insoluble in water*, as well as choosing a initiator which produces hydrophobic radicals. Use of a highly hydrophobic monomer for the modification of NRL means that radicals can only be formed in the NRL particles; moreover, because the monomer is highly hydrophobic, exit of radicals formed by transfer is minimal,<sup>10-12</sup> and aqueous-phase propagation of any exited radical to a sufficient degree of polymerisation to form a precursor particle is unlikely. All in all, secondary particle formation should be obviated.

One suitable hydrophobic monomers for this purpose is vinyl *neo*-decanoate (Veo Va-10<sup>®</sup> or Neo-10<sup>®</sup>). We have measured the solubility of this monomer in pure water as about  $4 \times 10^{-5}$  mol dm<sup>-3</sup>.

A procedure to implement this strategy is as follows<sup>9</sup>. The ammoniated NRL is swollen with the monomer (note that this requires some time,

since the low water solubility means slow transport across the aqueous phase). A suitable initiator is chosen, one example of which is cumene hydroperoxide (CHP) and tetraethylene-pentamine); the hydrophobic nature of the CHP ensures newly-generated radicals will be unlikely to be present in the water phase. A suitable surfactant is chosen such that coagulation of the NRL does not coagulate; appropriate surfactants can be chosen from the type used for synthetic rubber<sup>13</sup>. Polymerisation can be effected in a number of ways, including batch and semi-continuous (where the redox initiator is injected either in shots or continuously).

## RESULTS

In order to test for the absence of secondary nucleation, the procedure described above was performed on differentiated NRL, where smaller particles are removed by centrifugation: in the particular case here, the NRL sample used contained no particles smaller than 300 nm. The presence of new particles can then be detected by examining particle size distributions by both transmission electron microscopy and by capillary hydrodynamic fractionation (CHDF).

When an NRL was used as a seed for second stage growth with *styrene*, the particle size distributions showed extensive secondary particle formation. However, when the same procedure was followed with vinyl *neo*-decanoate, no particles smaller than the original NRL were observed, as expected from the preceding mechanism-based discussion.

The next test for the expected occurrence of extensive grafting is from an examination of the  $T_g$ . Particular care must be taken in the

technique used for this purpose. For this, we employ MTDSC (modulated thermal differential scanning calorimetry), where the modulated heating helps reduce artifacts due to kinetic rather than thermodynamic properties of the polymer. Figure 3 compares the thermograms so obtained for four different samples. (a) NRL without any artificial polymer, and three samples prepared by polymerising an artificial polymer as above, using (b) methyl methacrylate, and (c) vinyl *neo*-decanoate. The unmodified NRL and MMA-modified samples both show essentially the same  $T_g$ :  $-65.4^\circ\text{C}$  and  $-65.3^\circ\text{C}$  (the MMA sample also exhibits a much higher  $T_g$  corresponding to MMA, although that is not shown in the figure). This is as expected, since the MMA is sufficiently water-soluble that secondary nucleation is expected to occur readily. The  $T_g$  with the NRL samples wherein vinyl *neo*-decanoate was polymerised is however quite different:  $-60.9^\circ\text{C}$  (the mass of new polymer was about 10% of that in the NRL); again, a higher  $T_g$  was also seen in each case, corresponding to the second polymer. Moreover, the MTDSC trace does not return to the baseline between the two  $T_g$  maxima.

This increase in the  $T_g$  of the rubber polymer for this water-insoluble monomer is consistent with significant grafting having taken place, either as a (semi-)IPN or at least involving microphases of the two polymers.

#### RATE DATA

Rate data, obtained by dilatometry calibrated by gravimetry, show some unexpected behaviour. While MMA systems polymerise at similar rates to those seen in ordinary seeded emulsion polymerisations, vinyl *neo*-decanoate polymerises much more slowly, as shown in

Figure 4. This is despite the very high propagation rate coefficient of vinyl *neo*-decanoate, as measured by pulsed laser polymerisation<sup>14</sup>

This slow rate is not due to some peculiarity of the kinetics of seed emulsion polymerisation of vinyl *neo*-decanoate, since the rate of seeded polymerisation of this monomer in a butyl acrylate seed (which is of course also rubbery, like NRL) is quite fast. Possible reasons for the slow rate of this monomer in NRL compared to the fast rate of the other species may be one or all of the following reasons:

- (a) The radical species formed by initiator and vinyl *neo*-decanoate may be particularly reactive towards protein, and/or
- (b) This radical species may form a relatively stable species with the backbone double bond in natural rubber (*i.e.* unfavourable reactivity ratios), and/or
- (c) The grafting with vinyl *neo*-decanoate is so effective that the particles cannot swell fully when polymerisation has gone beyond a certain conversion, and so form a polyisoprene-rich core and a vinyl *neo*-decanoate monomer-rich shell, with very high rates of termination in the latter

Of these, (b) is unlikely, since the initial rate in Figure 4 is seen to be quite fast; this observation also suggests that (a) is unlikely. The high effectiveness of grafting which is suggested by the remaining explanation, (c) is consistent with the larger change in the  $T_g$  for vinyl *neo*-decanoate

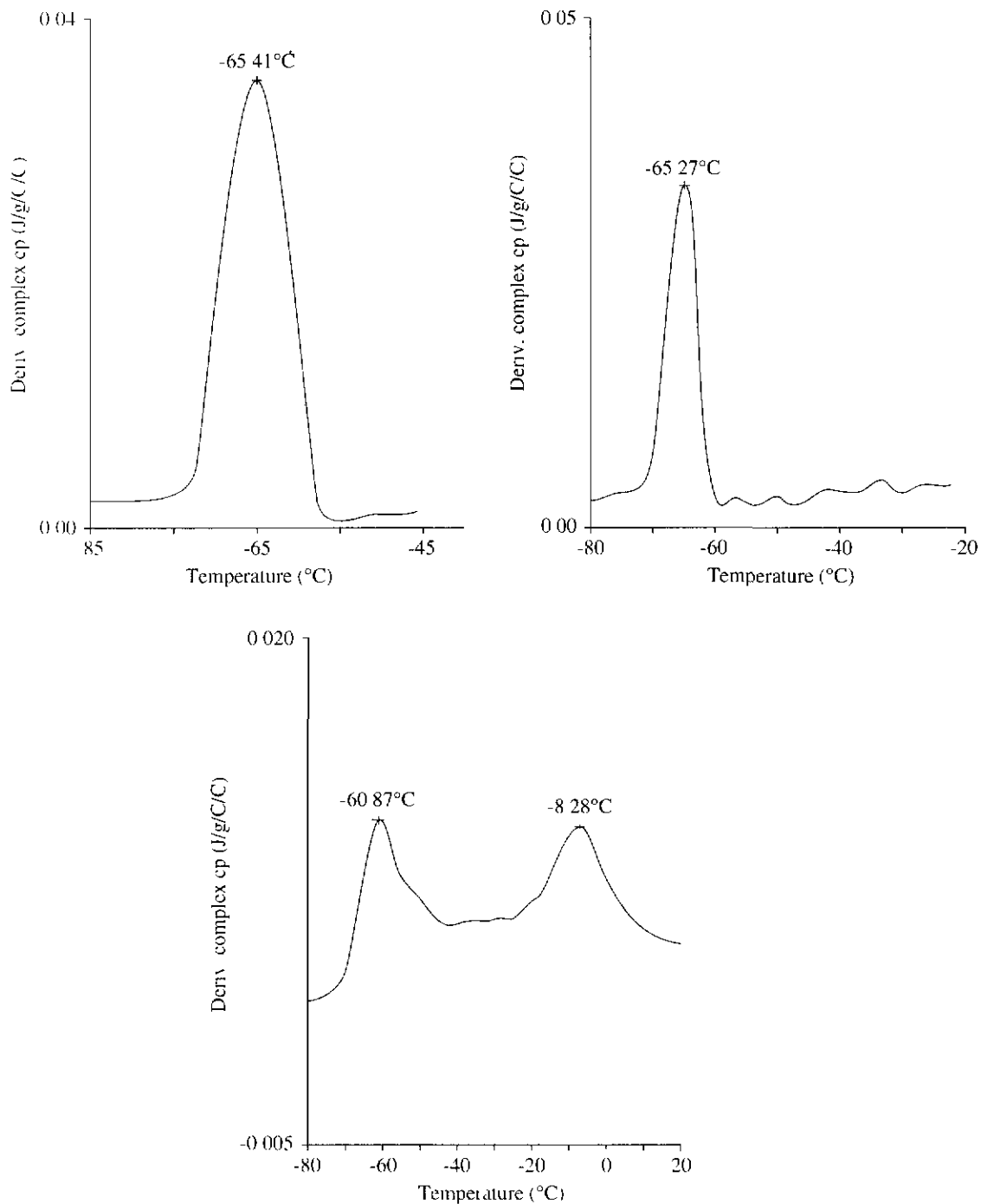


Figure 3 MTDSC thermograms of natural rubber, of NRL modified by seeded polymerisation with MMA, and of NRL modified by seeded polymerisation with vinyl neo-decanoate

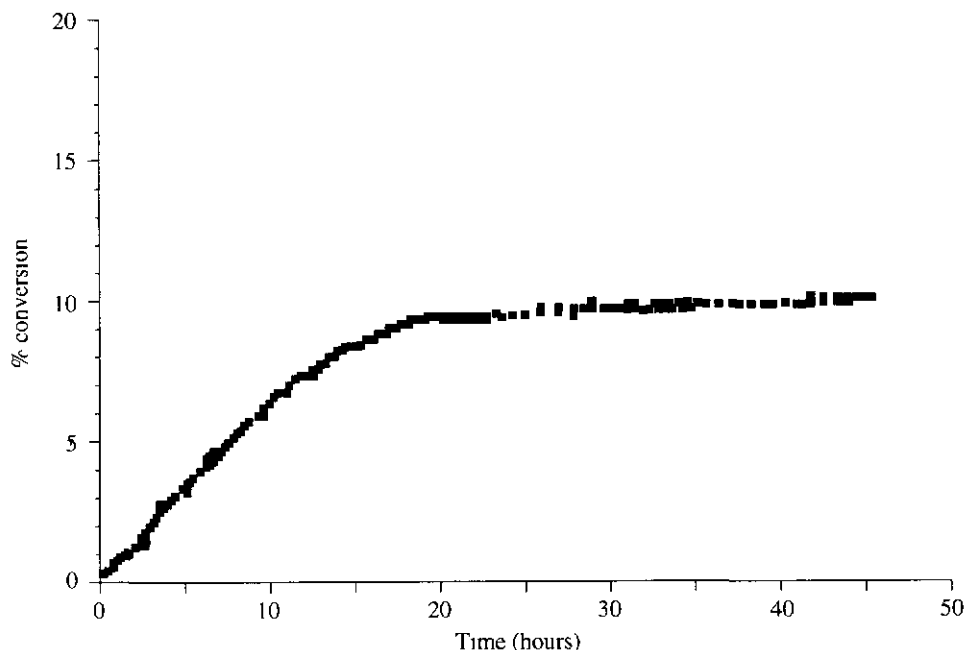


Figure 4 Conversion as a function of time for a 1:1 natural rubber + vinyl neo decanoate system  
initiator  $3 \times 10^{-4} \text{ mol dm}^{-3}$  persulphate plus 2% mercaptan at  $50^\circ\text{C}$

## CONCLUSIONS

The production of a modified ammoniated natural rubber latex by performing polymerisation with these latices as seed for growth with a highly hydrophobic monomer leads to a product where the  $T_g$  data are consistent with the formation of a relatively homogeneous (semi-)IPN or grafted micro-phases, as expected from mechanistic arguments based on the avoidance of secondary particle formation. There are some mechanistic questions which require further work, especially

the reason for the slow rate of polymerisation seen with vinyl *neo*-decanoate

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