Novel graft copolymers from mechanistically-designed seeded emulsion polymerization

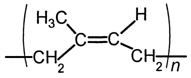
Nadaraja Subramaniam,[a] Michael J. Monteiro,[a] Joshua R. Taylor,[a]
Anne Simpson-Gomes[b], Robert G. Gilbert[a*]

[a]Chemistry School, Sydney University, NSW 2006, Australia
[b]Electron Microscope Unit , Sydney University, NSW 2006, Australia

SUMMARY: While natural rubber and natural rubber latex (NRL) have technical and environmental advantages, there are limitations in applications, which could be extended by creating a graft copolymer in the latex with artificial monomer(s) through the double bond on the *cis*-polyisoprene. Previous attempts to create such grafting through second-stage polymerization with the NRL as seed did not give uniform morphology of the resulting polymer, presumably because of insufficient grafting. This is overcome by combining two strategies: (a) the second-stage monomer system includes one or more components that are extremely water-insoluble, thereby avoiding secondary particle formation and subsequent imbibement, and (b) the second-stage monomer is chosen to have free-radical chemistry that can readily form graft sites with polyisoprene which undergo further propagation. One monomer that satisfies these criteria is lauryl acrylate, and indeed uniform morphology is observed in using this monomer polymerized with NRL as seed under appropriate conditions.

Introduction

Natural rubber latex (NRL) is a polymer colloid largely comprising *cis*-polyisoprene:



Some of the technical and environmental advantages of this substance include NRL being a renewable resource, and the polyisoprene, being essentially 100% *cis*, has a large increase in nominal stress at high deformation (e.g.,[1]). Extending the usage of NRL by being able to make graft copolymers of an artificial monomer, using the convenience of seeded emulsion polymerization[2], has obvious potential.

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The use of NRL as a seed to grow a second monomer inside the latex would seem a straightforward extension of conventional seeded technology$^{3)}$. However, attempts to use this method to make, e.g., block and/or graft copolymers, often fail. For example, if one takes natural rubber latex and attempts a second-stage polymerization of methyl methacrylate (MMA) therein, with the hope that extensive grafting will result through the double bonds of the polyisoprene, what is found$^{4)}$ is that most of the new PMMA forms in spatially separate domains (fruit-cake morphology, or "inclusions"), implying that little grafting can have occurred. However, one would expect that in a material which had extensive grafting between old and new polymer, the grafts would functions as *in situ* compatibilizer, and that therefore a material with extensive grafting would be more spatially homogeneous, perhaps forming microdomains of single chains. Such a material could have novel applications.

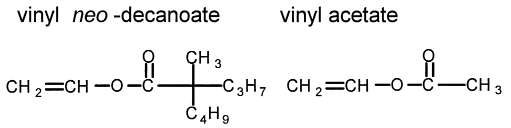
Mechanistic postulates

NRL comprises a highly polydisperse latex (average particle size ~1 μm), containing a large amount of added NH_3 to prevent bacterial attack during storage. The latex is stabilized by adsorbed long-chain fatty acids which are hydrolysis products of phospholipids; some colloidal stability also comes from polypeptides which arise from hydrolysis of the original proteins adsorbed on the surface$^{5)}$.

Based on fundamental polymerization mechanisms, we now suggest that two separate criteria must be obeyed to obtain extensive grafting by seeded emulsion polymerization in NRL.

Criterion 1: avoidance of secondary nucleation and imbibement

It has been postulated$^{6)}$ that one cause for the formation of inclusions arises because secondary nucleation occurs very readily in seeded emulsion polymerization of sterically-stabilized systems such as NRL. The reason for this ease of secondary nucleation are now emerging$^{7-9)}$: it is likely that the polymeric stabilizer forms a "hairy layer" around the particle, which slows down the entry of z-mers (radicals formed by aqueous-phase propagation which are of sufficient degree of polymerization to be surface-active, and thus enter the interior of a particle rapidly and irreversibly). These radicals may thus re-enter the aqueous phase rather than a pre-existing particle and then form new particles, i.e., cause secondary nucleation. The resulting small particles can be imbibed by the NRL, giving domains rich in the second-stage polymer; subsequent polymerization occurs preferentially in these domains. This problem can be overcome6) by using a monomer for the second-stage polymerization which is extremely water-insoluble. Secondary nucleation cannot occur if a water-insoluble monomer is used, since there is virtually no monomer in the water phase to form radicals which in turn could form new particles. One such monomer is vinyl *neo*-decanoate (VnD), which apart from its hydrophobicity has very similar chemistry to vinyl acetate:



$CH_2{=}CH{-}O{-}C({=}O){-}C(CH_3)(C_4H_9){-}C_3H_7 \quad CH_2{=}CH{-}O{-}C({=}O){-}CH_3$

(VnD is actually a mixture of branched isomers, one of which is shown above). This avoidance of secondary nucleation will be assisted by using an initiator system which does not produce aqueous-phase radicals. One suitable system6) is the redox system comprising cumene hydroperoxide, tetraethylenepentamine (TEPA) and trace amounts of Fe^{2+} found in NRL; this produces radicals at the particle-water interface.

Criterion 2: suitably reactive monomer

A necessity for the formation of extensive grafting by this technique is (a) that the second-stage monomer reacts readily with *cis*-polyisoprene (either by propagating with the double bonds or by chain transfer to polymer), and (b) that the radicals centres so formed on the pre-existing polymer chains themselves propagate readily. This is best illustrated by considering, for illustrative purposes, a monomer which would not be suitable for reasons of the wrong free-radical chemistry: vinyl acetate (this would also be unsuitable because it is relatively water-soluble). The vinyl acetate radical is very reactive: e.g., its propagation rate coefficient (k_p) is *ca*. 7×10^3 dm^3 mol^{-1} s^{-1} at 50°C10). However, vinyl acetate monomer is relatively unreactive towards other radicals: for example, it is well known that the presence of a small amount of styrene monomer inhibits the free-radical polymerization of vinyl acetate, because while the vinyl acetate radical reacts readily with styrene monomer, vinyl acetate monomer is unreactive towards the resulting styryl radical11).

Suitably reactive monomers, which should propagate readily as well as having reactive monomers, can be found among the acrylates. For example, butyl acrylate has an extremely high k_p [12,13] (the reasons for which are now understood on theoretical grounds[14]), a large transfer constant to itself [15] and the reactivity ratio with styrene[16] is about 0.5, i.e., butyl acrylate monomer reacts readily with styryl radicals.

The above two criteria suggest that uniform particle morphology should be obtained with monomers of low water solubility, such as VnD, lauryl acrylate (LA) or lauryl methacrylate (LMA). However, extensive grafting and complete polymerization are most likely to be obtained with a highly reactive monomer. Butyl acrylate is unsuitable because, while highly reactive, it is not highly insoluble in water (solubility ~ $6\text{x}10^{-3}$ mol dm^{-3} at 50°C [17]); however, quantum chemistry calculations of transition states[14] suggest that its high reactivity is likely to be shared by most acrylates. Hence LA should give extensive grafting, and should not show the extensive inclusions seen, for example, when NRL is used as a seed in the emulsion polymerization of MMA.

Designed synthesis

Two sets of experiments were performed based on the above mechanistic precepts: testing the radical-reactivity hypothesis through bulk experiments, and testing the homogeneity by appropriate seeded emulsion polymerization. All experiments were performed at 50°C.

A series of bulk polymerizations were carried out in the presence and absence of added polyisoprene. These were performed to separate effects peculiar to emulsion polymerization and/or to the unusual substances present in NRL (proteins, etc.) from those which arise because of the free-radical chemistry alone. Bulk experiments were carried out with 0.01 M AIBN as initiator. To examine the effects of pre-existing polyisoprene, it was necessary to use low molecular weight synthetic polyisoprene prepared in toluene with high initiator concentration (0.2 M *tert*–butylhydroperoxide). This is because (a) high molecular weight polyisoprene is insoluble in solvents such as VnD monomer, and (b) polyisoprene obtained from NRL may still contain small amounts of protein, etc., which are difficult to remove completely. This use of synthetic polyisoprene in bulk/solution polymerizations excludes sources of retardation from proteins, fatty acids and other impurities found in natural rubber latex. Conversion/time data were obtained for pure VnD, and VnD with varying amounts of added low-molecular-weight synthetic polyisoprene. Conversion was measured gravimetrically; because bulk VnD becomes very viscous above about 20% conversion, and the monomer cannot be readily removed by evaporation or extraction except at elevated temperatures when thermal polymerization can occur, conversion/time data were only obtained up to ~20 % conversion.

The procedure devised for the seeded emulsion polymerizations in NRL was as follows. NRL was swollen with the desired monomer; because transport through the water phase can be very slow with highly insoluble monomers, swelling was allowed to take place for 1 day. The (high-ammonia) NRL had a solids content of 57 %; the seeded polymerization system was designed to give a final solids content of between 10 and 15 % if the second-stage polymerization went to completion. Choice of surfactant is important, because NRL is not particularly colloidally stable, and coagulation can occur, e.g., with injudicious monomer addition. A suitable surfactant was found to be potassium oleate. As stated, it is desirable that the radical source not be in the water phase. Although one could in principle use a highly insoluble organic-phase initiator for this purpose, this usually requires a relatively high temperature (say, 50°C) which makes coagulation more likely. Although the present system did not show coagulation, this could possibly occur with subsequent scale-up, and the ability to go to lower temperatures might then be desirable. A redox couple was therefore chosen as the initiator system, since this could be run at a lower temperature if desired, with the components chosen such that radicals would be expected to be created largely at the particle-water interface: cumene hydroperoxide (lipophilic), tetraethylenepentamine (hydrophilic) and Fe^{2+}. The monomer-swollen NRL was swollen with cumene hydroperoxide, and TEPA added when the reaction mixture reached 50°C. Conversion was measured gravimetrically.

Rate data

Bulk polymerizations

Fig. 1 compares conversion as a function of time for bulk VnD to that obtained in the presence of varying amounts of added low molecular weight synthetic polyisoprene. Pure bulk VnD polymerizes quickly, reaching 20 % conversion in about an hour; this is in accord with simulations using conventional bulk kinetics and the measured[18)], very high, k_p for this monomer. Fig. 1 shows that the addition of polyisoprene results in a dramatic retardation.

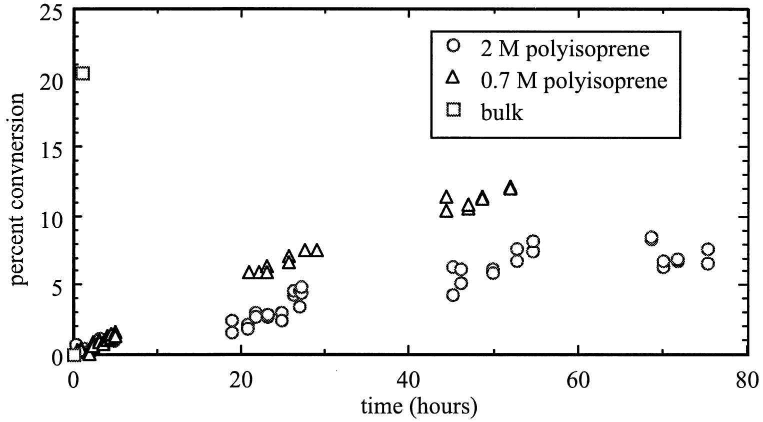
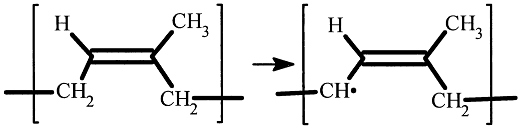


Fig. 1: Conversion as a function of time for VnD monomer with AIBN initiator at 50°C, in bulk and in the presence of various amounts of low molecular weight synthetic polyisoprene

One explanation for the dramatic retardation is retardative chain transfer, i.e. chain transfer in which some of the transferred radicals are slow to propagate and are lost through subsequent short-radical/radical termination. The reason for the slow propagation may well be the formation of an allylic radical by chain transfer from the (reactive) VnD radical:



This allylic radical is slow to propagate with the (unreactive) VnD monomer, exactly analogous to the styrene/vinyl acetate inhibition discussed above.

This inference also explains the observation[19)] that vinyl acetate (which has very similar radical chemistry to that of VnD) does not produce a significant increase in grafting when added to a system in which MMA is grown in an NRL seed.

Seeded kinetics

Consistent with the behaviour observed in bulk polymerization of VnD, low conversion is also observed when VnD is polymerized in bulk with NRL as seed: typically, 20% conversion is attained after 24 hours.

As stated, the two criteria for extensive grafting require a monomer that is both reactive and water-insoluble. An appropriate candidate is LA, since this monomer is much more reactive than VnD. Seeded emulsion polymerization of this monomer in NRL is indeed found to attain high conversion in a few hours. It is reasonable to suppose that this may arise because, while an allylic radical formed by grafting is slow to propagate with an unreactive vinyl ester, this radical nevertheless propagates quickly with a reactive acrylate.

Polymer properties: testing the hypotheses

The suppositions that seeded emulsion polymerization of water-insoluble monomers in NRL should produce extensive grafting and uniform morphology, with the amount of grafting and conversion both increased if these monomers are reactive (e.g., acrylates), were tested by two methods: DMA (dynamic mechanical analysis) to obtain dynamical mechanical response, and novel methods of electron-microscopy imaging to examine morphology.

DMA data

The DMA of the dried latex was obtained using a TA Instruments DMA 2980, and results are shown in Fig. 2. The maximum in these plots of tan δ as a function of temperature gives T_g. The $\mathrm{T_g}$ for natural rubber is – 49.8°C by this technique. Now, different values for T_g for NR are found by other methods: e.g., modulated-temperature DSC (MDSC) yields $T_g = -67.0°\mathrm{C}$. This apparent discrepancy is simply because different techniques measure different properties (MDSC measures heat capacity while DMA involves chain mobility); what is important is the comparison of appropriate data from the same method.

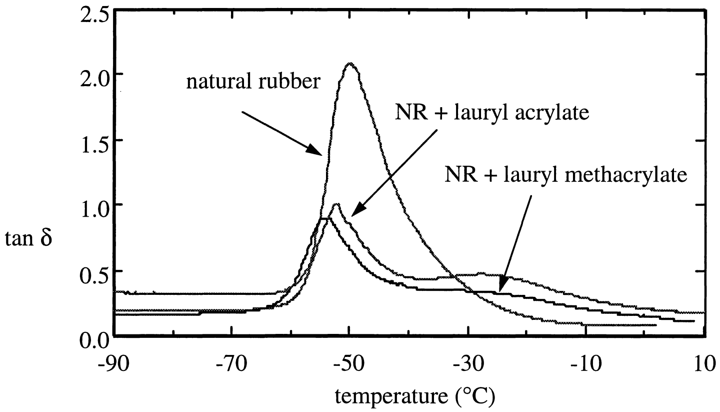


Fig. 2: DMA at 1 Hz for unmodified NR, and NR modified by second-stage seeded emulsion polymerization of LA and LMA

The results in Fig. 2 for the modified NRL (i.e., made by seeded polymerization of LMA and LA) are unexpected. The polymers formed by simple bulk homopolymerization of these monomers have T_g values measured by DSC of – 68.8 and – 67.7°C respectively. With the modified NRL containing these monomers, there is a slight shift in the T_g as measured by the maximum in tan δ. However, it is the very broad behaviour of the tan δ data outside the maximum that is revealing. This is indeed what is expected in a highly grafted system. The broadness is presumably caused by increased chain mobility at higher temperatures, which may reasonably be supposed to arise because the grafts are very long. That is, the tan δ data are consistent with extensive grafting for the acrylate and methacrylate systems.

Morphology by cryoscopic microtoming

One objective of the present study is to avoid the formation of inclusions in the seeded emulsion polymerization of NRL. Two alternative methods were developed to study the morphology of the particles in the modified natural rubber latexes. In the first method, the modified polymer was cooled below the T_g of natural rubber using liquid nitrogen. Ultrathin sections were then cut and the ultrastructure viewed by transmission electron microscopy after vapour-staining with OsO_4; extreme care is required in the slicing and sample manipulation. When applied to latexes made by polymerization of MMA in an NRL seed, the observed morphology showed inclusions, as also seen in an alternative imaging technique, viz., extrusion with a polystyrene matrix[4)], thereby verifying that cryoscopic microtoming gives an adequate representation of the true morphology.

Cryomicrotomy applied to latexes wherein VnD, LA and LMA were polymerized reveals particle morphologies which have not been previously seen. The particles with VnD and LA show spatial uniformity, as expected from the mechanistic arguments. Those with LMA show inclusions towards the edges of the pre-existing rubber. This latter observation suggests that grafting is less extensive with LMA, a not-unexpected result.

Morphology by fixing/epoxy microtoming

Cryomicrotomy is very time consuming. In an alternative method, the specimens are prepared by chemical fixation to compare with the ultrastructure found by cryomicrotomy. Glutaraldehyde and OsO_4 were used for chemical fixation; the sample was then dehydrated in ethanol, epoxy resin added, and cured in an oven. Microtoming was then performed with a glass knife. OsO_4 has been used routinely to stain rubber and as a biological fixation. Both glutaraldehyde and OsO_4 should preserve the ultrastructure of natural rubber as well as preserving protein around the natural rubber particle. This microtoming technique revealed morphologies very similar to those from cryoscopic microtoming. It is found that the chemical fixation method is not only faster than cryomicrotoming and reveals the particle morphology of the modified latex (including showing occluded morphology with MMA-modified latex), but also images the protein layer around the modified natural rubber particle. This might be useful in locating and identifying natural proteins in NRL which can cause allergic reaction in surgical gloves.

In both cases, electron microscopy indicates that the products using VnD and LA are spatially uniform (although tiny microdomains may still be present), in contrast to the process with MMA.

Conclusions

Rate, DMA and electron microscopy data of modified NRL are all consistent with extensive grafting occurring when the second monomer is highly water-insoluble (thereby avoiding secondary particle formation and subsequent imbibement) and having a highly reactive monomer (thereby going to high conversion). These studies show that a good understanding of the basic mechanisms of emulsion polymerization(2) can be used to make novel materials. It is also apparent that designing second-stage emulsion polymerizations to give particular properties can be achieved by study of the kinetics in these biocomposite systems.

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