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Using Mechanisms to Make Seemingly Impossible Latexes and Polymers

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SUMMARY: 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 (a) extensive grating between hydrophobic and hydrophilic entities, (b) sufficient graft copolymer is created *in situ* to compatibilize two polymers with significantly different solubility parameters, and (c) graft copolymers between styrene and aniline with interesting electrical properties.

Introduction

Growing polymers in dispersed media has many advantages (such as control of particle morphology, for example to make a core-shell latex), but also many restrictions. Thus controlling molecular architecture (e.g., making comb polymers) is hard (a) because the multiphase nature of the system means that hydrophobic compared to hydrophilic monomers and/or polymers tend to reside in different phases, and (b) because of the restrictions that occur in any free-radical polymerization (such as the simultaneous occurrence of transfer, termination and propagation). Of course, the origins of these difficulties are also often the reasons for many of the advantages of emulsion polymerization. However, by judicious choice of systems and through application of the basic mechanisms of emulsion polymerization1) and of free-radical polymerization2), it is possible to make some unusual polymers and latexes which turn these apparent liabilities into assets. Some goals might be: (a) making graft block copolymers from hydrophilic and hydrophobic monomers, (b) making polymer blends containing sufficient graft copolymers to achieve spatial homogeneity between incompatible species, and

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(c) making blends of conducting and nonconducting polymers. All of these have potential uses as new materials.

To achieve these goals, it is necessary to design the system based on both the free-radical and emulsion polymerization chemistry. For example, if it is desired to make a latex wherein there is extensive grafting of hydrophobic and hydrophilic monomers, then an appropriate initiator system would be one that produces radicals at the particle-water interface. One possibility is a reactive surfactant of the type explored extensively by Guyot and others$^{3-5)}$. An alternative method used here is a judicious choice of redox couple to exploit the *topology* of systems undergoing (seeded) emulsion polymerization. That is, one can force radicals, radical source and monomers to be in certain locations. The initiator and/or monomers must be chosen so that the desired grafting process is optimized. Furthermore, if extensive grafting is required, homopolymerization of any component should be kept to a minimum; this in turn requires that secondary particle formation must be obviated (which could otherwise result in one component being solely in the new particles).

The implementation of this philosophy will be illustrated through three examples of polymerization in dispersed media, each of which creates a novel material. The generic strategy is the familiar process of seeded emulsion polymerization.

Free-radical chemistry

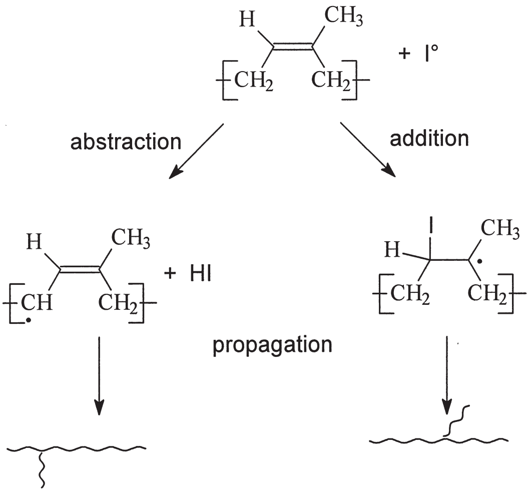
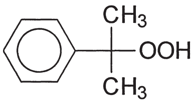


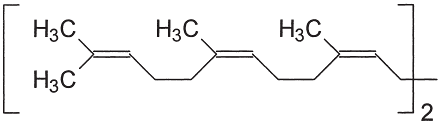
Fig. 1. Reaction scheme for abstraction and addition to *cis*-polyisoprene

A strategy which will be employed here in several ways is though use of a seed in an emulsion polymerization where the pre-existing polymer has a backbone which can readily undergo abstraction (of labile hydrogens) or addition (through residual double bonds) to form a grafting site. An example is polyisoprene (polybutadiene can equally well be used), which can undergo either addition or abstraction with a radical I° (which may be a species arising from an initiator), as shown in Fig. 1. The abstraction pathway may be facilitated through the stability of the resulting allylic radical. By the same token, the stability of the radical may mean that it could have a very slow reinitiation rate coefficient with some monomers, e.g. monomers such as vinyl ethers where the radical is reactive but the monomer is not. Thus it is well known that the free-radical polymerization of vinyl acetate is strongly retarded by the presence of styrene, because the latter results in a relatively stable benzylic radical which has a low reactivity with vinyl ether monomers. This is despite the fact that the vinyl ether *radical* is quite reactive, as evidenced by the high values of the propagation rate coefficients for vinyl acetate[6] and vinyl *neo*-decanoate[7]. On the other hand, *acrylates* have both reactive monomers and reactive radicals : for example, butyl acrylate has very high rate coefficients for both propagation[8-9] and for transfer (abstraction)[10].These facts will later be used to advantage to create the right sort of grafting sites.

Bulky initiator radicals, such as those from cumene hydroperoxide:



in a redox system tend to favour abstraction compared to addition (see for example data for the *t*-butoxyl radical[2]). A series of nitroxide-trapping experiments to verify this was performed using squalene, which is a 30-carbon analogue of polyisoprene :

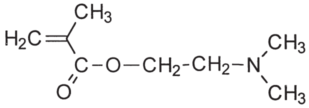


Squalene has a boiling point of 285°C, and is readily recovered from benzene. Squalene is small enough to allow the use of reverse-phase HPLC for separation of the products from the nitroxide trapping experiment, but also long enough to reasonably describe the polymeric nature of polyisoprene. In these studies, benzoyl peroxide was used as thermal initiator and TEMPO as radical trap. Benzoyl peroxide thermally decomposes to give two bulky electrophilic radical fragments (in contrast to the nucleophilic nature of the cumyloxyl radical). The trapped species (alkoxyamine products) resulting from the reaction of the nitroxide with a carbon-centred radical are stable, can be isolated by HPLC, and their structure elucidated by NMR^11)^. The fractionation involved an initial partial separation of the products with 100 % methanol, and the fractions obtained were further purified with water and methanol (5-15 % w/w water). Diastereomers were not separated under these HPLC conditions, but addition and abstraction to the different chain positions were identified. In this preliminary work it was found that the addition reaction was reduced by a factor of six moving from the terminal double bonds to an internal double bond. The abstraction rate coefficient is three times larger than that for the addition to the internal double bonds, even for the highly reactive and electrophilic benzyloxyl radical. These results verify that for polyisoprene and cumene hydroperoxide, the dominant mechanism is hydrogen abstraction.

Another series of experiments was carried out to obtain the rate coefficients for the abstraction process involving vinyl *neo*-decanoate (VnD) and polybutadiene.12) The presence of small amounts of low molecular weight polyisoprene13) or polybutadiene results in a dramatic retardation in the bulk free-radical polymerization of VnD. Extensive rate data on this retardation for VnD and polybutadiene were fitted by assuming a mechanism of retardative chain transfer, whereby an alkanoate radical undergoes hydrogen transfer with polybutadiene, leaving an unreactive radical species (probably allylic in character) which cannot propagate and instead undergoes termination with another radical. The data yield Arrhenius parameters for the transfer step as $k_{\mathrm{tr,P}} = 10^{6.1}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}\ \exp(-\ 25.7\ \mathrm{kJ\ mol^{-1}}/RT)$, which, although subject to high uncertainty, are consistent either (a) with the rate-determining step being diffusion to a hindered butadiene unit of the chain end of an alkanoate macroradical, or (b) the actual (chemically-controlled) hydrogen transfer event, which would then have to have an unusually low activation energy. The Arrhenius parameters so obtained can be used subsequently to optimize conditions for creating graft copolymers with VnD as a grafting agent. It is useful to note the relatively low activation energy, which implies that grafting by this method should be effective over a wide temperature range.

Creating an extensively grafted copolymer of hydrophobic and hydrophilic monomers

The system chosen is isoprene and DMAEMA (dimethylaminoethylmethacrylate), a water-soluble monomer :



$$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}N(CH_3)_2$$

The objective is to create a latex with extensive grafting between this monomer and polyisoprene. This could be achieved if allylic radicals were formed on the polyisoprene backbone, which would subsequently undergo propagation with the DMAEMA monomer. Simply polymerizing a water solution of DMAEMA using persulfate and a polyisoprene seed would result in extensive formation of DMAEMA homopolymer in the water phase due to the unfavourable partitioning of monomer and initiator with respect to the polyisoprene. Hence the following approach was adopted. First, the initiator chosen was a redox couple: cumene hydroperoxide (CHP), which at low temperatures has low water solubility, and tetraethylenepentamine (TEPA), which is hydrophilic; these may also require the presence of tiny amounts of Fe^{2+} in the water phase to produce extensive radicals14). At the reaction temperature (~ room temperature) the CHP is partitioned to a significant extent inside the particles whilst the TEPA resides in the water phase. Essentially it is predicted that the formation of radicals will occur at the particle-water interface where the two components of the redox couple meet. The cumyloxyl radical should be located in region where there is a high concentration of polymer chains and also where there exists some concentration of DMAEMA, as suggested in Fig. 2. It is recognized that the efficiency of this initiation system is probably low, as the cumyloxyl radical can diffuse into the particle (away from the surface). It is postulated that the secondary nitrogen radical which is formed on the TEPA as a result of the redox interaction acts as a terminator of growing DMAEMA chains in the aqueous phase. The failure of unprotonated secondary radicals to react with double bonds (even at high temperatures ca. 150 °C) is well documented15). Seeded emulsion polymerization was carried out on a natural rubber (*cis*-polyisoprene) high-ammonia seed latex and DMAEMA monomer, in a 500 mL glass reactor with paddle stirrer under a nitrogen atmosphere. The reaction was

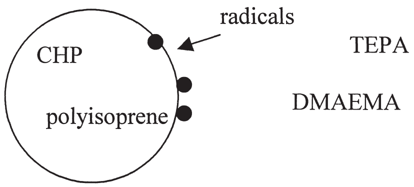


Fig 2. A redox initiator comprising a water-soluble part (TEPA) and water-insoluble part (CHP) results in radical creation at the particle interface, which is also the only region where polyisoprene and DMAEMA monomer can interact.

performed at room temperature with a stirring speed of 100 revolutions per minute. More details are given in Table 1.

Table 1: Recipe for the modification of NRL with DMAEMA.

	NRL 60 %w/w	DMAEMA	CHP	TEPA 10 %w/w	NH_3 0.5 %w/w
Mass (g)	250	37.5	0.625	2.65	209.75

The DMAEMA was added to the NH_3 solution and then to the NRL with the CHP. This mixture was stirred and purged with nitrogen gas for 1 hour. TEPA was added slowly with a syringe pump over the course of 5 hours. The reaction was allowed to run for almost 24 hours to ensure significant conversion of the monomer. The low temperature necessitates a long reaction period due to the slow reaction rates.

The result is a latex with unusual properties. For example, natural rubber latex is only marginally colloidally stable (it is always used with the addition of ammonia and has a pH of 10), and coagulates at $p\text{H} \lesssim 8$. However, a latex modified as above is extremely stable, even at $p\text{H} = 2$. Changing the reaction temperature results in an increase in the shear viscosity of the latex, which is attributable to the increase in water-soluble polymer formed (the increased solubility of CHP and the increased likelihood of TEPA propagating are postulated as reasons).

Electrophoretic measurements (Fig. 3) show a complete charge reversal on the surface of the modified particle. The isoelectric point occurs at approximately pH 6 with a very slow transition from negative to positive zeta potential. The isoelectric point has shifted one *p*H unit to the right in comparison to untreated NRL, which becomes positively charged at *p*H 5. The transition for pure NRL is also a good deal sharper than the DMAEMA modified latex.

Such results may come from an extensive graft copolymer of DMAEMA and polyisoprene, probably with a comb architecture. Of course, this is merely a postulate which must tested by proper analysis, e.g. by appropriate NMR. Other explanations might for example be unusual effects of any (ungrafted) polyDMAEMA, a possibility which can be checked by further experimentation.

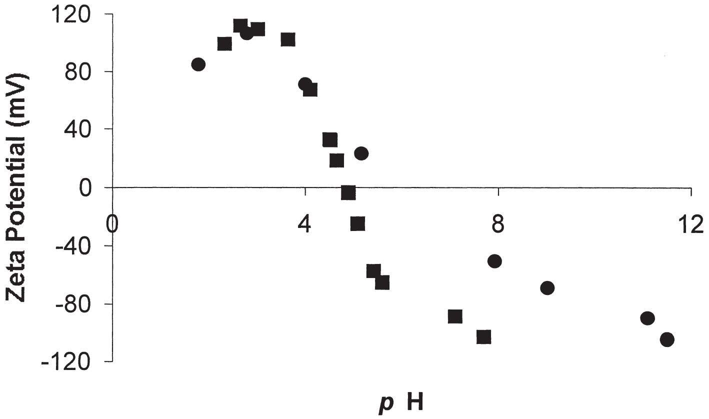


Figure 3: Electrophoretic measurements on NRL (squares) and modified NRL (circles)

Creating spatially-homogeneous copolymers

We have shown previously[13,16] that it is possible to grow spatially-homogeneous copolymer systems with a seed comprising a polymer on which grafting sites can be initiated, such as polyisoprene or polybutadiene, and a second-stage monomer such as VnD or lauryl acrylate (LA). Achieving spatial homogeneity requires special conditions when the solubility parameters δ of the two polymers differ significantly. Now, calculation of δ using group additivity[17] shows that one expects polyisoprene and pLA to be incompatible. Under such circumstances, two criteria must be satisfied to obtain a spatially homogeneous particle, as follows.

- It is necessary to avoid secondary nucleation during the second-stage growth, or else the secondary particles which form will be subsequently imbibed within the seed particles forming nuclei for subsequent second-stage growth. Conditions for avoiding secondary particle formation can be deduced by taking account of the mechanisms of particle formation1). In a system in which the surfactant concentration in the continuous phase is maintained below the cmc, the means by which secondary particles form is through homogeneous nucleation: propagation of aqueous-phase radicals to the critical degree of polymerization j_{crit} to undergo a coil-to-globule transition (i.e., to precipitate). This can be avoided by choosing the second monomer to be highly water-insoluble

- The second criterion which must be satisfied is to have sufficient grafting between pre-existing seed polymer and new polymer during the second-stage growth to create internal compatibilizers. This can be achieved through appropriate design of the free-radical chemistry: e.g., the second-stage monomer being sufficiently reactive to undergo propagation from graft sites such as the allylic ones which can arise with abstraction from polyisoprene or polybutadiene (Fig. 1). It should be noted that addition of polymeric radicals to the disubstituted and trisubstituted double bonds on the polybutadiene and polyisoprene, respectively, is slow, and thus abstraction should be favoured.

An important aspect of the characterization of the morphology of the resulting polymers is through electron microscopy, which is especially difficult for these rubbery polymer colloids. Two techniques have been designed for this purpose18-19). One of these, chemical fixing ultra-microtomy19), is relatively easy to implement. Glutaraldehyde is added to the latex, followed by OsO_4; the sample is then dehydrated in ethanol, epoxy resin then added; the sample cured in an oven, followed by ultramicrotoming with a glass knife and imaging with transmission electron microscopy. Applied to natural rubber latex samples in which methyl methacrylate has been polymerized, a “fruit-cake” (inclusion) morphology is clearly seen, in accord with the morphology seen with alternative, but much more laborious, techniques18,20).

As published elsewhere13), uniform morphology is observed in using LA polymerized with natural rubber latex as seed under appropriate conditions; LA satisfies the two criteria of being water-insoluble and being able to readily propagate from the type of radical resulting from abstraction in polyisoprene. Dynamic mechanical analysis (DMA) data also suggest extensive grafting, as expected from the free-radical chemistry. Typical experimental conditions are natural rubber latex as seed at $p\text{H} = 8$, potassium oleate as surfactant, CHP and TEPA as redox initiator, and a temperature of 50°C.

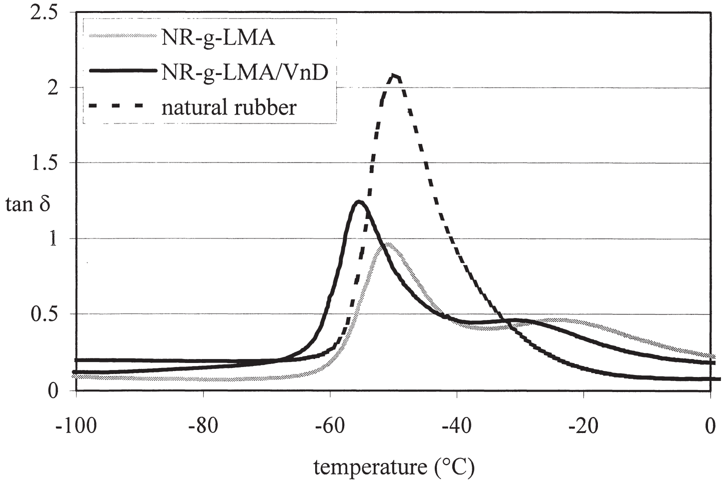


Fig 4. DMTA data for unmodified natural rubber latex, and latex modified with LMA and LMA plus VnD

On the other hand, this spatial uniformity is not seen in electron micrographs if the second-stage polymer is lauryl methacrylate (LMA); it is postulated that this is because LMA monomer is not as reactive as LA: significant inclusions are seen in the second-stage seeded polymerization of LMA in natural rubber latex. As shown above, the polymerization of VnD in the presence of polybutadiene shows clearly that retardative chain transfer occurs, i.e., that the VnD forms grafting sites on the pre-existing polymer which do not undergo further propagation with this unreactive monomer. The experiments just cited suggest that grafting could be increased by adding VnD. Indeed, addition of some VnD results in a much more homogeneous particle morphology. However, DMA thermograms shown in Fig. 4 suggest extensive branching has occurred both with and without the VnD. The increased homogeneity with some VnD may be ascribed either to increased grafting or possibly to increased compatibility arising from VnD/LMA copolymers, since the solubility parameter of polyVnD (calculated using additivity rules and the Fedors parameters for cohesive energy and molar volume group contributions21)) is close to that of polyisoprene.

Composite aniline-styrene polymer colloids

Aniline is a conducting polymer which can be made as a colloid[22-23)], and there are many potential applications for such materials, e.g., in electrostatic dissipation[24)]. Composites of these conducting polymers with non-conducting ones also have potential applications, for example in increasing processability. Armes and co-workers[25-26)] have developed means of making such composites based on non-conducting polymers as seeds in emulsion polymerization. We present here a methodology for the reverse procedure: using a polyaniline (PAN) colloid as a seed in which to polymerize styrene. One objective of this is to attain an intimate blend through grafting during the second-stage polymerization; in turn, it is essential to avoid secondary nucleation of polystyrene particles during the second stage. Using a PAN seed takes advantage of the fact that aniline can act as a transfer agent for styrene free-radical polymerization, which in turn can lead to formation of a graft copolymer. The process was based on means of avoiding new nucleation which mechanistic understanding is bringing about[27-28)]. The PAN seed colloid was grown with an emulsion consisting of a water phase of poly(vinyl alcohol) solution and an oil phase of organic solvent (e.g., toluene), plus aniline and a surfactant which functions both as emulsifier and dopant. After forming the emulsion, hydrochloric acid was added, followed by the oxidant, ammonium persulfate. Under appropriate conditions, the PAN is formed through a miniemulsion polymerization, yielding spherical particles; the original emulsion breaks at high conversion, yielding an organic and a water phase, with the latter containing a stable PAN colloid. Second-stage growth of this PAN seed with styrene was performed by first removing any inhibitor in the PAN seed using appropriate reagents[29)], then adding sodium hydrogencarbonate solution. The initiator was 2,2'-azobis(2-amidino-propane) dihydrochloride; sodium dodecyl sulfonate was added as surfactant, at a final concentration below the critical micelle concentration. The reaction was carried out at 65°C for over 20 hours. This gives a latex which is pale green rather than the dark green of PAN, and wherein the composite polymer has greatly reduced solubility in organic solvents such as toluene compared to both pure PAN and pure polystyrene. These changes suggest grafting and subsequent cross-linking have occurred. The UV/visible spectra shown in Fig. 5 are for a seed PAN latex and the composite grown from this, with particle sizes measured by photon corelation spectroscopy, PCS. These spectra show a major change in the electronic structure of PAN in the composite. The conductivity of the composite is also found to be greatly reduced from that of the parent PAN. The dielectric constant of this novel material is found to be strongly frequency-dependent, and to increase with the conductivity of the composite.

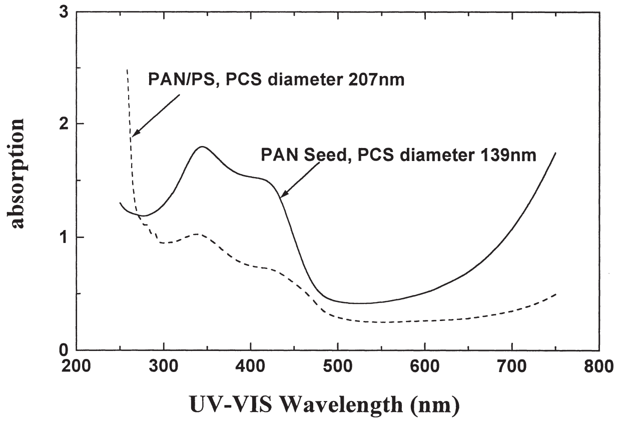


Fig. 5. UV spectra of PAN seed and of composite latex grown from this.

Conclusions

Unusual new materials, both polymer colloids and the polymer isolated from these, can be designed and synthesized by combining appropriate free-radical and emulsion-polymerization mechanistic knowledge. It is possible to make ìimpossibleî latexes by taking advantage of the discrete topology in polymerization in dispersed media, in combination with the right free-radical chemistry. These new materials have considerable potential application, for example, in extending uses of natural rubber for pressure-sensitive adhesives, surgical gloves and so on.

Acknowledgements

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