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Functionalization of Polymers by Metal-Mediated Processes

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I. Introduction

Polymers with controlled degrees of functional groups at a desired polymer chain length are useful building blocks for custom designing specialty polymer systems. Catalytic reactions on template polymers which produce polymer products with the desired density of one or more functional groups are one method of synthesizing these unique polymer building blocks.[1] For example, key connector groups[2] catalytically placed on a template polymer can aid in attaching other polymer chains or monomer groups in order to achieve the desired assembly.

This review will summarize the progress that has been achieved in transforming olefin containing polymers, such as polybutadiene (P(bd)), into key building blocks for specialty polymers via metal-mediated processes. This review focuses on catalytic reactions on polymers and complements earlier reviews on chemical modification of polymers[3−5] which examine research involving both catalytic and noncatalytic modification of unsaturated polymers.

Polybutadiene is a starting material for the majority of research papers cited in the present review. P(bd)'s availability at various molecular weight ranges and well-defined microstructures makes it a practical choice for catalytic modification.[6] By catalytic reactions on the P(bd), a functional group can potentially be placed on each butadiene unit (eq 1).

(1)

The evenly distributed carbon−carbon double bonds in P(bd) can be viewed as chemical handles on which polymer connector groups can be catalytically attached. Considering the strategy of adding various functional groups on a polymeric substrate by sequential catalytic reactions, there is a potential for transforming base polymers, such as P(bd), into specialized systems with a reasonable degree of flexibility. These polymers with a fixed number of functional groups are a useful addition to the materials available for the assembly of specialized systems.

Specifically this review focuses on the catalytic tools that have been useful in functionalizing olefin-containing polymers. Information on catalyst selectivity and controlled functional density will be highlighted as well as several examples that reveal more about the interactions of catalysts with polymer chains. Finally, examples are given of some complex polymer systems that have been assembled from this technology.

II. Nomenclature of Polybutadienes

Since a significant number of examples in this review describe the functionalization of polybutadienes, it is appropriate at this point to discuss the nomenclature used for describing the various forms of polybutadiene. Polymerization of butadiene can yield three isomeric polymer structures:[7] 1,2-units, *cis*-1,4-units, and *trans*-1,4-units (Figure 1). The degree of stereoregularity in primarily 1,2-polybutadienes can lead to three stereoisomeric forms[8] (Figure 2). When the R groups of the monomer units are all above (or below) the plane of the polymer backbone fully extended in a zigzag fashion, an *isotactic* polymer is formed. If the R groups alternate above

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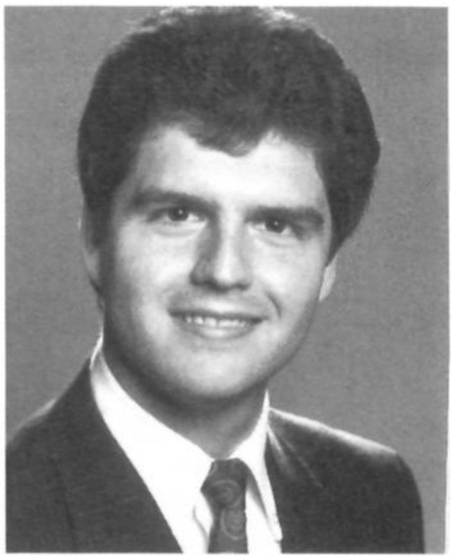
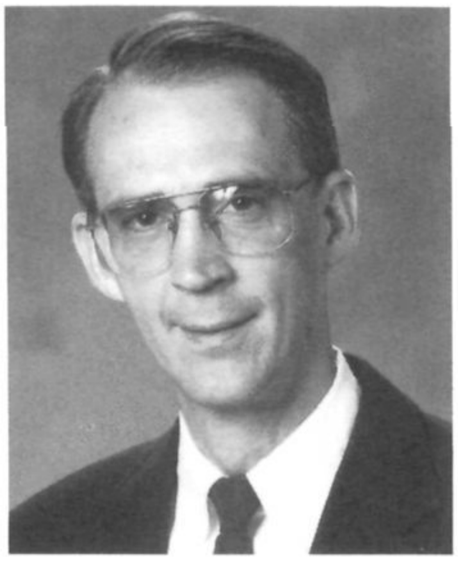
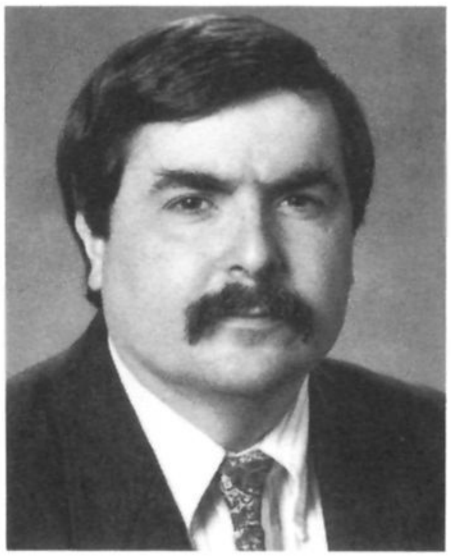


Martin McGrath was born in New York, NY, in 1963. He received his undergraduate degree with Distinction in Chemistry from the University of Pennsylvania in 1985 where he did undergraduate research with Alan G. MacDiarmid in the area of electrically conductive polymers. He received his graduate education in organometallic chemistry at Yale University under the direction of Robert Crabtree where he studied the stereochemistry of small molecule addition to square planar iridium complexes. He joined Monsanto in 1990 and is presently a Research Specialist in the Chemical Sciences Department of Monsanto Corporate Research. His research interests include metal catalyzed functionalization of polymers, site specific drug delivery systems, and the development of novel plastic intermediates and rubber additives.

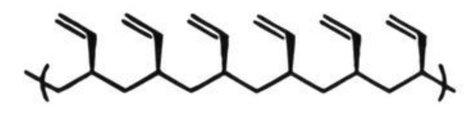


Erik Sall was born in Bethesda, MD, in 1952. He received his undergraduate degree with Distinction in Chemistry from the University of Virginia. He received M.S. and Ph.D. degrees in Chemical Engineering form Purdue University, where he studied oxygen transport phenomena under the direction of George Tsao. He joined Monsanto in 1982 and is presently a Senior Research Specialist in the Chemical Sciences Department of Monsanto Corporate Research. His research interests include mathematical modeling and stochastic processes.

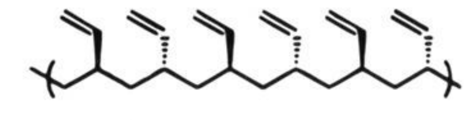


Samuel Tremont was born in Syracuse, NY, in 1950. He received a B.S. degree in Chemistry from LeMoyne College. He received his graduate education at the University of Rochester (1971–1975) under the direction of Christopher Dalton where he examined the mechanistic pathways associated with the photochemistry of γ,δ-unsaturated ketones. After postdoctoral work with Robert Bergman at the California Institute of Technology in Organometallic Chemistry, he joined Monsanto. Presently he is a Senior Fellow in the Chemical Sciences Department of Corporate Research. His research interests include developing new metal-mediated organic methods, controlled metal-catalyzed functionalization of polymers and site-directed delivery of drugs.

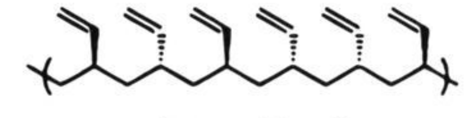
Figure 1.



isotactic 1,2-polybutadiene



syndiotactic 1,2-polybutadiene



atactic 1,2-polybutadiene

Figure 2.

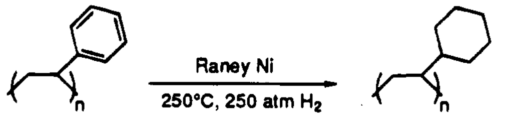
and below the plane of the polymer backbone, then the polymer is referred to as *syndiotactic* and if the R groups are randomly situated above and below the polymer plane, then the polymer is *atactic*. In the literature, 1,2-units have often been referred to as vinyl groups and *cis*/*trans*-1,4-butadiene units have been called internal olefins. For consistency, the different groups in polybutadienes will be referred to as 1,2-units and *cis*- and *trans*-1,4-units.

III. Hydrogenation

Quantitative hydrogenation of unsaturated polymers, prepared by controlled polymerization, provides a means of synthesizing saturated polymers with controlled molecular weights, microstructures, and stereochemistries that might not be available through monomer polymerizations alone.[9] For example, polymerization of vinylcyclohexane produces primarily isotactic, head-to-tail poly(vinylcyclohexane), but atactic, head-to-head poly(vinylcyclohexane) can be produced by the hydrogenation of poly(2,3-diphenylbutadiene) (see ref 13 below).

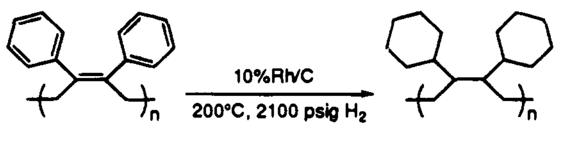
A. Heterogeneous Catalysts

The hydrogenation of polystyrene has been reported as far back as 1929.[10,11] More recently this problem was investigated in 1967 by Elias and Etter.[12] High molecular weight (M_w = 353000) polystyrene was hydrogenated in decalin using Raney Ni as a catalyst. Complete hydrogenation was achieved with temperatures of 250–270 °C and pressures of 3675–3822 psia and reaction times of 24 h. Hydrogenation was also accompanied by significant chain degradation. The molecular weight of the hydrogenated product was reported to be 61900 compared to 353000 for the starting material (eq 2).



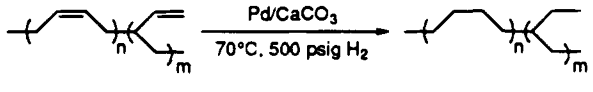
(2)

In 1978, Helbig *et al.*[13] reported the production of poly(vinylcyclohexane)s by the hydrogenation of poly(2,3-diphenylbutadiene) and polystyrene to produce head-to-head poly(vinylcyclohexane) and head-to-tail poly(vinylcyclohexane), respectively. Hydrogenations were carried out in decalin using 10% Rh on carbon as the catalyst at 200 °C and a reaction pressure between 2115 psia and 1915 psia for 4 h. Complete hydrogenation of the backbone double bonds and the phenyl rings of the polymers was reported (eq 3).



(3)

In 1979, Rachapudy[14] compared the homogeneous hydrogenation of 8% 1,2-polybutadiene using alkylated transition metal salts with heterogeneous hydrogenation using nickel on kieselguhr or palladium on calcium carbonate (eq 4). Only the heterogeneous catalysts were found to give completely hydrogenated products without catalyst fragments becoming attached to the chain during hydrogenation and appearing in the final product. Conditions for heterogeneous hydrogenation were reported to be 715 psia of hydrogen, 150 °C and 3–4 h for nickel on kieselguhr and 515 psia of hydrogen, 70 °C and 3–4 h for palladium on calcium carbonate. Physical properties of the hydrogenated polybutadiene were found to be similar to those of commercially available branched polyethylene.

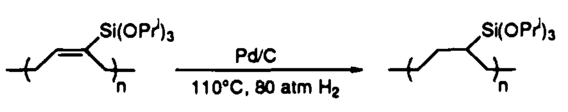


(4)

Palladium on calcium carbonate was also used by Zhongde *et al.*[15a,b,9] to hydrogenate polybutadienes, polyisoprenes, and poly(1,3-dimethyl-1-butenylene) to their saturated counterparts for physical property measurements.

In 1984, Gotro and Graessley also used Pd/CaCO$_3$ to hydrogenate polyisoprenes.[16] Hydrogenation of 1,4-polyisoprene provides a poly(ethylene-*co*-propylene) polymer with an alternating ethylene–propylene microstructure. The physical and rheological properties of hydrogenated 1,4-polyisoprene were found to be good models for the properties of 1:1 ethylene/propylene copolymers.

In 1990, Takenaka *et al.*[17] found Pd on carbon (Pd/C) to be the hydrogenation catalyst of choice for poly(2-silyl-substituted-1,3-butadiene)s (eq 5). Takenaka *et al.* found that Pd/C was capable of hydrogenating a variety of silyl-substituted polybutadienes made from polymerization of (2-trialkoxysilyl-substituted-1,3-butadiene)s at 110 °C and 1176 psia of hydrogen. Hydrogenation with Rh(PPh$_3$)$_3$Cl, Wilkinson's catalyst, gave back only unreacted starting material. Presumably the steric bulk of the trialkoxysilyl group prevents the coordination of Rh(PPh$_3$)$_3$Cl to the double bonds of the polymer and thereby prevents hydrogenation by this catalyst. Hydrogenation with Pd/C appears to be unaffected by the steric bulk of the silyl groups.



(5)

In 1988, Rosedale and Bates[18] published some interesting results concerning the mechanism of 1,2-polybutadiene hydrogenation with Pd/CaCO$_3$. It was found that hydrogenation with Pd/CaCO$_3$ under 515 psia of hydrogen and 70 °C proceeded at first to hydrogenation of 85% of the double bonds present and then a slower reduction of the remaining double bonds. This first reduction to 85% saturation does not proceed through a random hydrogenation of all of the double bonds on all of the polymer chains. Hydrogenation takes place to 85% conversion on each polymer chain in a single step. At less than 85% conversion for the total reaction mass, the reaction mixture consists of a certain percentage of polymer chains that have been reacted to 85% saturation and the remainder is unreacted polymer. On the basis of the results of their work and other absorption data for olefins on palladium surfaces, Rosedale and Bates conclude that the entire polymer chain adsorbs to the palladium surface and is hydrogenated until approximately 85% conversion at which point there are not enough olefins left on the polymer to effectively hold it to the catalyst surface and the polymer is desorbed in favor of an unreacted polymer molecule.

In 1993, Gehlsen and Bates[19] report the hydrogenation of polystyrene, polyisoprene, and polystyrene-polyisoprene block polymers with two different heterogeneous palladium catalysts, Pd–CaCO$_3$ and Pd–BaSO$_4$. Polyisoprene and polystyrene were fully saturated with either Pd–CaCO$_3$ at 105 °C or Pd–BaSO$_4$ at 140 °C under 515 psia of hydrogen. Polyisoprene was saturated to poly(ethylenepropylene) and polystyrene was fully saturated to poly(vinylcyclohexane). In the case of the polystyrene-polyisoprene block polymers at 105 °C, Pd–CaCO$_3$ provided only incomplete saturation while Pd–BaSO$_4$ gave a completely saturated product. By using heterogeneous catalysts under mild conditions, Gehlsen and Bates report that fully saturated polymers could be obtained without chain degradation. It was noted that in order to allow the heterogeneous catalysts to provide a fully saturated product under mild conditions, a special reactor had to be built to minimize mass transfer effects that limit heterogeneous catalysts in typical commercial reactors. The design of this new reactor is to be published in a separate article.

In 1989, Wideman and Hsu[20] patented a hydrogenation catalyst consisting of polymer-bound Rh(I) groups for the hydrogenation of olefin-containing polymers. The catalyst was synthesized by brominating macroreticular styrene/divinyl benzene resin beads and then reacting the brominated beads with ClPPh$_2$ and Li to functionalize the resin beads in the 4-position of the styrene units with diphenylphosphino groups. The pendant diphenylphosphino groups were then used as ligands to coordinate to a Rh(I) compound making polymer-bound Wilkinson's catalyst, polymer$-PPh_2-Rh(PPh_3)_2Cl$. The polymer-bound Wilkinson's catalyst was found to hydrogenate the 1,4-double bonds of polybutadiene preferentially over the 1,2-double bonds. This is opposite to the reactivity displayed by the soluble $Rh(PPh_3)_3Cl$. Wilkinson's catalyst usually hydrogenates 1,2-butadiene groups much more quickly than 1,4-groups; however, when the rhodium catalyst is bound to a polymer support, the selectivity is reversed and the reduction of 1,4-double bonds is favored. No explanation was provided in the patent for this interesting change in reactivity.

In a departure from typical heterogeneous catalysts, Pittman, Lewis, and Habib[21] report the hydrogenation of cis-1,4-polybutadiene by "soluble" metal oxide particles. Air oxidation and distillation of water from a mixture of metal hydroxides and metal carboxylates generated metal oxides particles surrounded by a carboxylic acid layer. The metal oxide particles remain intact, and the carboxylic acid layer provides "solubility" in a variety of organic solvents, such as mineral spirits, hexane, and benzene. Soluble NiO particles (122 Å) activated with $AlEt_3$ (Al/Ni = 3.5) were capable of completely saturating *cis*-1,4-polybutadiene at 120 °C under 125 psia hydrogen after 10 h. The solubilized nickel oxide particles were unable to hydrogenate polyisoprene.

Recently, a short review by Murio discussing many industrial applications for the hydrogenation of polymers was published in *Chemical Catalyst News* issued by Engelhard Corporation.[22] A majority of references in Murio's review were taken from the Japanese Patent literature.

B. Homogeneous Catalysts

1. Metal Salts

In 1966, Hassell and Shaw disclosed in a South African patent[23] the hydrogenation of polybutadiene-polyisoprene-polybutadiene block copolymers using nickel acetate activated by triethylaluminum in a ratio of 1:1.5 nickel/aluminum at 140 °C and 1515 psia of hydrogen to produce polyethylene-poly(ethylenepropylene)-polyethylene block copolymers.

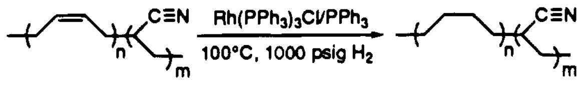
A subsequent report of homogeneous catalysts used for the hydrogenation of olefin containing polymers by Tikhomirov *et al.* in 1969[24] describes the hydrogenation of polybutadienes with chromium(III) acetylacetonate activated by triisobutylaluminum. Hydrogenation of *cis*-1,4-polybutadiene, polybutadiene made by sodium metal-initiated polymerization (BUNA rubber), 1,2-polybutadiene, and styrene-butadiene copolymers using $Cr(acac)_3/Al(i\text{-}Bu)_3$ was demonstrated at a variety of conditions, 40−100 °C, 15−809 psia H_2, 2−12 h. Residual unsaturated in the products ranged from 3−20%. Tikhomirov determined from reaction kinetics and IR evidence that the hydrogenation of random microstructure polybutadiene proceeds in a two-step fashion: 1,2-butadiene units are hydrogenated first and then the 1,4-butadiene units are hydrogenated.

Selective hydrogenation of olefin-containing polymers by cobalt(II) 2-ethylhexanoate activated by either triethylaluminum or *n*-butyllithium was described by Falk in 1971.[25] An aluminum to cobalt ratio of 3.45:1 produces a catalyst system that will selectively hydrogenate 1,4-butadiene units without hydrogenating the 1,4-isoprene units in 1,4-butadiene-1,4-isoprene-1,4-butadiene block and random copolymers. In the case of the *n*-butyllithium-activated system, selectivity for hydrogenating 1,4-butadiene units in the presence of 1,4-isoprene units occurs at a lithium to cobalt ratio of 5.0:1. Hydrogenations in both the triethylaluminum- and *n*-butyllithium-activated cobalt systems were performed with 0.3 mol % catalyst at 50 °C in alkane solvents under 65 psia hydrogen pressure.

In 1979, Camberlin *et al.*[26] also used metal salts activated by alkylaluminum to hydrogenate polybutadienes. Several hydroxy-terminated polybutadienes and unfunctionalized polybutadienes at a variety of molecular weights were hydrogenated using nickel or cobalt carboxylates and triethylaluminum, 120 °C, and 305 psia of hydrogen. Hydrogenation was taken to different levels (10−100%) and the physical properties of the polymers, such as T_g and viscosity, were determined at the various levels of unsaturation. In general, the glass transition temperature, T_g, decreased and the viscosity increased with increasing amounts of hydrogenation in the polymers.

2. Rhodium-Based Catalysts

By far the most widely used homogeneous hydrogenation catalysts for polyolefin reduction are rhodium(I)-based catalysts. In 1972, Finch[27] reported the hydrogenation of acrylonitrile-butadiene copolymers with $RhCl(PPh_3)_3$ and added PPh_3 in chlorobenzene at 100 °C and 1015 psia for 8 h. This catalyst system reduced the double bonds without affecting the nitrile groups to provide a saturated polymer with pendant nitrile groups (eq 6). Acrylonitrile-butadiene copolymers with a mostly alternating microstructure of acrylonitrile-butadiene units corresponding to a run number of greater than 92 and a mole percent of acrylonitrile between 47% and 53% and molecular weights in the range of 20000 to 1000000 were reported to show large increases in tensile strength upon saturation.



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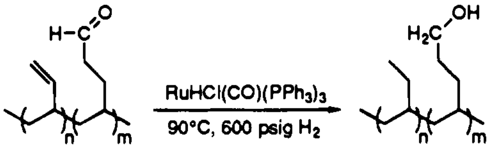
In 1975, Krause[28] disclosed the hydrogenation of oil-insoluble styrene-butadiene latexes using $RhCl(PPh_3)_3$. The styrene-butadiene latexes were swollen in benzene to allow the catalyst to get into the matrix and then the polymers were hydrogenated at temperatures ranging from 22 °C to 65 °C under 455−815 psia of hydrogen for 3−36 h. Residual unsaturation as low as 0.3% was achieved. Reactions run without a swelling medium, such as benzene, did not show any hydrogenation. Hydrogenated latexes showed an increase in thermal and UV stability when compared to unsaturated starting materials.

$RhH(PPh_3)_3$ has been used by Rempel and Azizian[29] in the presence of added ligand, PPh_3, and without added ligand to hydrogenate acrylonitrile-butadiene copolymers. In the first case, the copolymer would be dissolved in a solvent, such as chlorobenzene, and a ligand to catalyst ratio of 10:1 would be used. The reactions were run at temperatures of 90–130 °C and under a hydrogen pressure of 406 psia for 1–15 h. Up to 99+% hydrogenation could be achieved. In the second case, the same acrylonitrile-butadiene copolymers could be hydrogenated with $RhH(PPh_3)_3$ without any added ligand. The reactions were performed in chlorobenzene under milder conditions, 10–200 psia hydrogen, 40–85 °C, and for 2.5–19 h. Complete hydrogenation could be achieved using these conditions as well.

There have been several reports of hydrogenation of polybutadienes and butadiene-acrylonitrile copolymers using $RhCl(PPh_3)_3$ since the mid1980s. In 1986, Mohammadi, Ling, and Rempel[30] reported the use of $RhCl(PPh_3)_3$ for the hydrogenation of polybutadiene. Hydrogenations were carried out in toluene at 60 °C under 75 psia of hydrogen. By monitoring gas uptake, polymers with different degrees of unsaturation (0–100%) were prepared. This paper also reports the reduction of polybutadiene aldehydes made by the hydroformylation of polybutadiene. The reduction was accomplished using $RuHCl(CO)(PPh_3)_3$ in toluene at 90 °C under 615 psia of hydrogen. The ruthenium catalyst reduced both the aldehyde groups and the double bonds to yield a saturated, hydroxymethylated product (eq 7).



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In 1986, Doi *et al.*[31] reported the hydrogenation of 1,4-, atactic 1,2-, and syndiotactic 1,2-polybutadienes to prepare saturated polymers with well-defined molecular weights and microstructures. Polymerization of 1-butene provides primarily isotactic poly(1-butene) while hydrogenation of the atactic and syndiotactic 1,2-polybutadienes provides a means of forming atactic and syndiotactic poly(1-butene). Hydrogenations were done in toluene using $RhCl(PPh_3)_3$ and PPh_3 (Rh/P = 19:1) at 100 °C under 740 psia of hydrogen for 24 h. The thermal properties and structural analysis by ^{13}C NMR were reported.

In 1987, Mohammadi and Rempel[32] describe the hydrogenation of acrylonitrile-butadiene copolymers using $RhCl(PPh_3)_3$. The copolymers are fully hydrogenated in 2-butanone at 20–50 °C under less than 15 psia of hydrogen. No reduction of the nitrile groups is apparent. Analysis of the hydrogenation kinetics indicates that the nitrile groups compete with the double bonds for coordination to the metal center of the catalyst since at higher acrylonitrile to butadiene ratios, the hydrogenation reaction is slower. In addition, the presence of the nitrile groups appears to stabilize the catalyst and prevent formation of the inactive dimer, $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$. Also on the basis of the reaction profile, $RhCl(PPh_3)_3$ does not show any selectivity for 1,2- vs 1,4-butadiene units in the copolymer when 2-butanone is used as a solvent.

In 1989, Mohammadi and Rempel[33] provided a kinetic and mechanistic study of the hydrogenation of polybutadiene with $RhCl(PPh_3)_3$. Reactions were done in toluene at 20–50 °C at pressures below 15 psia of hydrogen. The reaction is first order in [Rh], [C=C], and $[H_2]$ at low $[H_2]$. At higher $[H_2]$, the reaction is zero order in $[H_2]$. The catalyst also showed a selectivity for 1,2-butadiene units over 1,4-butadiene units. This study was followed in 1990 by Guo and Rempel[34] who determined that $RhCl(PPh_3)_3$ also shows a faster rate for hydrogenation of *cis*-1,4-butadiene units over *trans*-1,4-butadiene units. These hydrogenations were performed in *o*-dichlorobenzene at 65–125 °C and 0.6–15 psia of hydrogen. Guo and Rempel[34] also show that hydrogenation of monodispersed polybutadiene can be used to make monodispersed poly(ethylene) or poly(ethylene-*co*-butene) standards for gel permeation chromatography.

In 1989, Bouchal, Ilavský, and Žůrková[35] studied the kinetics of hydrogenation of hydroxy terminated polybutadienes using $RhCl(PPh_3)_3$. It was found that at high conversions (98% saturation) there was a partial loss of hydroxy end groups. The loss of functional groups could be minimized by lowering the catalyst concentration, the reaction temperature, and the partial pressure of hydrogen.

In 1991, Bhattacharjee, Bhowmick, and Avasthi[36] report the high-pressure hydrogenation of acrylonitrile-butadiene rubber using $RhCl(PPh_3)_3$. Optimum conditions reported were a catalyst concentration of 0.02 mmol, 812 psia of hydrogen, and 100 °C in chlorobenzene for 11 h. Analysis of the product shows complete hydrogenation of the C=C double bonds and no reduction of the nitrile groups. These reaction conditions appear to be optimum for acrylonitrile-butadiene rubbers containing 40–51% acrylonitrile content. At lower acrylonitrile content or with polybutadiene, less than 100% hydrogenation is obtained.

3. Palladium-Based Catalysts

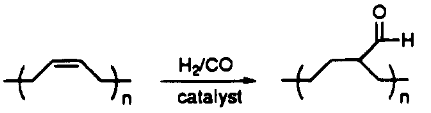
Previously in 1990, Bhattacharjee, Bhowmick, and Avasthi[37] reported the hydrogenation of acrylonitrile-butadiene rubber using $[\{Pd(2\text{-benzoylpyridine})(OAc)\}_2]\cdot 0.25\ CH_2Cl_2$ as the catalyst. The reactions were done in chloroform at 50 °C under 102 psia of hydrogen for 3–20 h. This system was used to hydrogenate the nitrile rubbers to different degrees of saturation at which point the physical properties of the polymers were determined. The T_g of the nitrile rubbers decreased after hydrogenation. The hydrogenated nitrile rubbers displayed an increase in tensile strength compared to the starting polymers. Green strength, breaking strain, and small strain modulus all increased upon hydrogenation. The palladium catalyst used is selective for C=C double-bond reduction since no evidence of nitrile reduction was present in any of the hydrogenated polymers.

4. Solventless Hydrogenation

In 1989, Gilliom[38] reported the hydrogenation of polybutadiene and butadiene-styrene triblock polymers without the presence of a solvent using either Wilkinson's catalyst, $RhCl(PPh_3)_3$, or Crabtree's catalyst, $[Ir(COD)(PMePh_2)_2]PF_6$ (COD = 1,5-cyclooctadiene). The dispersion of the catalyst through the polymer was achieved by dissolving the polymer and the catalyst in an appropriate solvent, such as toluene or dichloromethane, and then removing the solvent under vacuum. The resulting polymer/catalyst mixture (9.1% by wt catalyst) was then placed under 55 psia of hydrogen and heated to 60 °C. On the order of 80−94% conversion was achieved with both catalysts in under 70 h. Lower catalyst loadings were also investigated. $RhCl(PPh_3)_3$ at 1.1% by wt catalyst loading was reported to afford 88% hydrogenation of the double bonds in a butadiene-styrene triblock polymer after several days reaction.

IV. Hydroformylation of Olefin Polymers

Hydroformylation of polymers refers to the reaction of pendant or backbone olefin elements of the polymer with a suitable catalyst in the presence of "syngas", i.e. some mixture (usually 1:1) of carbon monoxide and hydrogen to produce aldehyde groups on the polymer:



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As will be seen below, hydroformylation is often performed as a means of providing sites for further derivation to, for example, hydroxymethyl groups.

It is well known that hydroformylation can be catalyzed by group VIII metals. All of the patent and open literature work reviewed here specify Co or Rh catalysts. It is a reaction of some industrial importance, most notably the Co-catalyzed reactions to produce the so-called "oxo-alcohols". These applications have been well reviewed by Falbe[39] and are exemplified in a patent issued to Natta *et al.*[40] for the hydroformylation and hydrogenation of *monomer* substrates in the presence of Co (as dicobalt octacarbonyl). The potential value of extending hydroformylation to oligomeric or polymeric substrates is reflected in the fact that much of the work in this area is also published in the form of patents.[41−51] The recent dates on some of these patents indicates that industrial interest in hydroformylation of polymers continues.

A. Cobalt-Based Catalysts

We note first that Co-catalyzed hydroformylation can suffer from a lack of specificity due to a potential to simultaneously reduce aldehydes to alcohols and to isomerize or hydrogenate residual unsaturation in the substrate. For a polymeric substrate these undesirable side reactions of cobalt-catalyzed hydroformylation can lead to high MW, gelled material unless special precautions are taken.

For example, Ramp *et al.*[52] applied conditions similar to that of Natta et. al.[40] to the dicobaltoctacarbonyl-catalyzed hydroformylation of 1,4-polybutadiene, high styrene SBR (styrene-butadiene copolymer), and a number of other olefinic polymers. Typical reaction conditions were 145−180 °C, 2415 psia of 1:1 CO/H_2 synthesis gas, and ca. 5000 ppm Co (with respect to polymer and as $[Co(CO)_4]_2$). They found gelation of the products to be a significant problem and in many cases resorted to using a variety of condensing agents, such as glycol, to form acetals with the aldehydes generated on the polymer in order to prevent them from partaking in cross-linking reactions. They also found that high concentrations of low molecular weight, monomeric aldehydes (6:1 with respect to olefin) would produce a nongelled material. This led them to speculate that aldehyde polymerization was the main cause of product gelation. Gelation problems were mitigated somewhat in the hydroformylation of high styrene SBR (styrene/butadiene mole ratio 1:1), but acetal forming agents were needed here also for high conversions. For both high styrene SBR and 1,4-polybutadiene, all attempts to perform reductive hydroformylation by forcing the conversion of aldehydes to alcohols resulted in gelled material. They conclude that any combination of conversion level and polymer concentration leading to aldehyde concentrations in excess of 1×10^{-4} mol/mL is prone to gel.

In the 1960s a patent assigned to Esso Research and Engineering[46] and a subsequent series by Mertzweiller, Tenney, and Cull[47−51] described the preparation and performance of new phosphine and phosphite Co complexes which were claimed to be more active and selective in the hydroformylation of olefins. The general formula of the phosphine Co complexes employed is $[Co_2(CO)_6(PR_3)_2]$ (R is an alkyl radical with 1 to 6 carbons) and $[(C_nH_{2n-1})Co(CO)_y(PR_3)]_x$, in which n is 4−10, x is 1 or 2, and y is 1 or 2 such that when x is 1 then y is 2 and when y is 2, x is 1. The phosphite Co catalysts conform to the general formula $(C_nH_{2n-1})Co(CO)_2[(R_zA)_x\text{-}P\text{-}R_y]$, in which A is oxygen, R is selected from hydrogen or alkyl groups having 1 to 6 carbon atoms, x is 1−3, y is 3 − x, and z is 1 or 2.

The bulk of this patent series was aimed at polymeric substrates and addressed various aspects of a two-step reductive hydroformylation of polymers to produce a fully hydroxylated, variably hydrogenated material. Hydroformylation is favored in the first step, performed at 515−1215 psia synthesis gas, 150−200 °C, and 500−5000 ppm Co (with respect to polymer). They claimed that under these conditions the ligand-stabilized catalyst is less active toward hydrogenation and aldehyde reduction. The second stage of the reaction is performed with the same catalyst but under somewhat more severe conditions, such as 190−220 °C and 1015−1515 psia hydrogen (with a small CO pressure to stabilize the catalyst), leading to complete reduction of the aldehyde functionalities to hydroxymethyl and rapid hydrogenation of the residual unsaturation in the polymer. They also note performance differences between the phosphine and phosphite versions of their catalyst complexes, namely, (1) an apparent tendency of the phosphite catalyst to yield double bond isomerization in the first reaction step and (2) a tendency of the phosphite catalyst to hydrogenate residual double bonds in preference to the carbonyls in step 2.

The Mertzweiller, Tenney, and Cull patents contain examples of the hydroformylation of several polymeric substrates and also note several instances of gelation problems. They ascribed these problems to intermolecular acetal formation between aldehyde and hydroxymethyl groups (formed from the aldehydes), an indication that the desired specificity during the hydroformylation step was not complete. This problem was mitigated[50] by the addition of large excesses of monomeric primary alcohols to the reaction solvent either before of after reaction.

Winkler and Neumann[42] extended the hydroformylation by Co–phosphine complexes to styrene-butadiene block copolymers to produce copolymers containing hydroxymethyl groups and in which the residual double bonds had been fully hydrogenated. They noted that materials of high 1,2-butadiene microstructure led to products that were poor elastomers and in many cases showed a tendency to gel during recovery. They also note that lactone, ester, and ketone formation are known for this reaction and had to keep polymer concentrations below 5–10% in order to prevent gelation. Oxygen incorporation was limited to 6–8% for this reason also.

Recently, Di Serio *et al.*[53] report the hydroformylation of a low molecular weight "commercial" poly(isobutene) (MW = 442) in the presence of a cobalt acac (acac = acetylacetonate) catalyst and triphenylphosphine cocatalyst at temperatures from 130 to 155 °C, pressures of 1795 to 3015 psia, and 3.5 to 8.5 wt % Co (with respect to polymer). Reactions were performed both in solution (20 wt % polymer) and on neat polymer, and timed samples were obtained and analyzed for intermediates by NMR. It was found that aldehyde was formed during the early stages of the reaction but its level decreased as it was converted to alcohol as the reaction proceeded. There is no mention of gel formation. They observed that vinyl and monosubstituted vinyl react in series. Mathematical expressions for predicting the conversion to aldehyde and alcohol based on series rate expressions were developed and used to derive rate constants. They claim that the series reaction effect arises from steric factors involving the catalyst complex and olefin bond type, and that this reflects a "partitioning of cobalt among the different olefins".

As the above examples show, Co-catalyzed hydroformylation of olefinic polymers is often accompanied by unwanted and gel producing side reactions unless performed in the presence of stoichiometric amounts of agents that intercept the aldehyde as it is formed.

B. Rhodium-Based Catalysts

Much more active and selective chemistry is available from Rh complexes. Sanui *et al.*[54] were the first to report the Rh catalyzed hydroformylation of polymers. They employed $HRh(CO)(PPh_3)_3$ to hydroformylate polypentenamer (<1% vinyl) up to 50% conversion using 1:1 H_2/CO syngas at quite moderate pressure (55–315 psia), and temperature (25–40 °C). Polymer payloads, however, were only ca. 2 wt % in toluene. Reaction rate increased with temperature and pressure. Rate also increased with H_2-rich synthesis gas mixtures (2:1) but minor amounts of hydrogenation and isomerization were observed under these conditions.

Azuma *et al.*[55] extended this work to include 1,4-polybutadiene substrate. They experienced gelation problems with dried material that had been hydroformylated in excess of ca. 30%. They go on to describe a number of chemical agents, such as sodium borohydride, used in stoichiometric amounts for reduction of the formyl groups formed by hydroformylation.

Mohammadi *et al.*[30] and Mohammadi and Rempel[56] describe the synthesis and characterization of hydroformylated polybutadiene using $HRh(CO)(PPh_3)_3$, 1:1 H_2/CO syngas, and 45 psia total pressure at 60 °C. Materials of 2–20% conversion were produced for a high vinyl (90% 1,2-butadiene units), M_n = 30000 starting polybutadiene. They also discuss IR and NMR methods for characterizing the hydroformylated product. Their studies indicate that the Rh catalyst system used produced hydroformylation of 1,2-vinyl groups in predominantly the anti-Markovnikov position. They attribute this to steric factors. In a separate paper[57] they describe a computer-automated reactor for performing real-time quantification of syngas uptake from a calibrated reservoir which provides a high degree of control over the extent of reaction.

Tremont *et al.*[58] and Mills *et al.*[59] describe $HRh(CO)(PPh_3)_3$-catalyzed hydroformylation of 1,2-syndiotactic polybutadiene (M_n = 21800), 1,4-*cis*-polybutadiene (M_n = 67910), and a mixed polybutadiene (M_n = 5200) in toluene and in the presence of excess triphenylphosphine. Reactions were performed at 315 psia of 1:1 H_2/CO synthesis gas, 80 °C, and a PPh_3/Rh ratio of ca. 165. Kinetic information was obtained by tracking syngas uptake from a calibrated reservoir supplying gas to the reactor across a pressure regulator. NMR and MW analysis of the products were performed. They found that addition of aldehyde was not biased toward any particular weight fraction of their polymers, which suggests that the active catalyst does not remain attached to any one polymer chain for extended periods. High selectivity to aldehyde product was confirmed by agreement between gas uptake calculations and NMR analysis of the products. Kinetic data showed that initial rates for the syndiotactic 1,2-polybutadiene were ca. 6 times faster than those for the 1,4-substrate. They were able to model the behavior of the mixed 1,2-, 1,4-polybutadiene by a composite rate equation assuming pseudo-first order with respect to both of these components.

Sibtain and Rempel[60] extended earlier work with polybutadiene to include Rh-catalyzed hydroformylation (and Ru-catalyzed hydroxymethylation) of styrene-butadiene copolymers. Detailed kinetics and product analysis for similar systems were later reported by Scott and Rempel,[61] who concluded that the diphosphine complex $HRh(CO)(PPh_3)_2$ is the catalytically active species. Constant reactor headspace composition was taken as evidence of no hydrogenation under their reaction conditions (typically 51 °C, 13 psia 1:1 H_2/CO, $[HRh(CO)(PPh_3)_3]$ = 2.08 mM, [olefin units] = 444 mM, toluene solvent). Both internal and pendant olefins were hydroformylated, although maximum conversion in toluene was only 30% of the available double bonds. Vinyl olefins were hydroformylated exclusively to the anti-Markovnikov addition product. Addition of excess PPh_3 (0 to ca. 8-fold molar excess with respect to catalyst) slowed the reaction down but had no observed effect on selectivity. The hydroformylation exhibited first-order kinetics (with respect to olefin) only through the first 5% of the reaction. (This is to be compared to the previously mentioned accounts of Tremont *et al.*[58] and Mills *et al.*[59] in which it was found that a mixed 1,4-, 1,2-polybutadiene system could be described by a first-order model up to ca. 40% conversion in a system with a 165-fold excess of PPh_3, with respect to catalyst.) Interestingly, maximum conversion (in toluene) was only ca. 30% for a series of styrene-butadiene copolymers, including random and block microstructures. For one copolymer studied this could be increased to ca. 50% using methyl isobutyl ketone as a solvent.

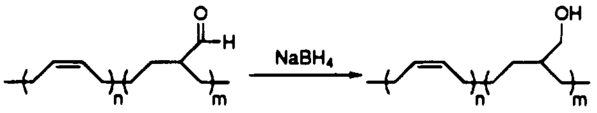
Forster *et al.*[45] and McGrath *et al.*[62] describe the use of $Rh(acac)(CO)_2$ (acac = acetylacetonate) to hydroformylate a low molecular weight EPDM polymer (Mn = 5000, EPDM = *e*thylene *p*ropylene *d*iene *m*onomer polymer) with as little as 10 ppm Rh (with respect to polymer) in toluene (100 °C, 1015 psia 1:1 H_2/CO). For polybutadiene substrate, however, $Rh(acac)(CO)_2$ exhibited severe deactivation, and so $HRh(CO)(PPh_3)_3$ (no excess phosphine) was used instead. The high selectivity of the Rh-catalyzed reaction was again confirmed by excellent agreement between gas uptake, ^1H NMR of aldehyde product, and ASTM OH analysis (ASTM E222) of the polyols formed from the polyaldehydes made. This study also notes the ability of both $Rh(acac)(CO)_2$ and $HRh(CO)(PPh_3)_3$ catalysts to hydroformylate EPDM polymer in solventless, simulated melt phase conditions. $HRh(CO)(PPh_3)_3$ was more active in this case.

Rhodium-catalyzed hydroformylation of olefinic polymers offers an excellent opportunity to pursue some of the kinetic and statistical aspects of polymeric reactions (described in a later section). This is due to (1) the extremely high selectivity for this reaction, (2) the "constant" concentration at a given pressure of syngas in the reaction solution (which removes it from the mathematical manipulations), (3) the ability, by withholding catalyst until initial temperature and pressures are reached, to precisely determine the start time of the reaction and hence improve the accuracy of the kinetic analysis, and (4) the ability to collect instantaneous, high-quality conversion vs time data through calibrated gas uptake measurements. Such considerations have already been touched upon in the kinetic analyses of Tremont[58] and Rempel[60] and co-workers. It would be interesting to examine the solvent effects on rate reported by Scott and Rempel[61] in terms of the sequence distribution, if a way to do this could be found. It is necessary for such studies, of course, for the activity of the catalyst to remain constant over the course of the reaction. This assumption may be more appropriate for the PPh_3-stabilized systems.

C. Reductions of Polyaldehydes

1. Chemical Methods

Reduction of hydroformylated polyolefins can allow for the production of polyols with hydroxymethyl groups distributed along the polymer chain instead of just at the termini. Some early work using homogeneous cobalt catalysts[52] suffered from a lack of selectivity and cross-linking of the final product. We will limit ourselves to some of the more recent work which has provided soluble, stable polyol products. In 1980, Azuma *et al.*[55] reported the reduction of hydroformylated polypentenamers and polybutadienes using sodium borohydride or sodium trimethoxyborohydride as a reductant. Benzene solutions of the hydroformylated polymer were added to THF solutions of the borohydride reductant containing a certain amount of ethanol and stirred for 18–20 h. The reaction mixture was hydrolyzed with acetic acid and the polymers were recovered by precipitation with methanol. Although soluble products could be obtained from the hydroformylated polypentenamers using this method, a considerable amount of a cross-linking was encountered upon reduction of hydroformylated polybutadienes with sodium borohydride-based reagents to make polyols. McGrath *et al.*[62] report that $NaBH_4$, in the presence of an adequate proton source, was effective at reducing both EPDM and polybutadiene polyaldehydes to polyols without significant cross-linking (eqs 9 and 10). Reductions were performed by dissolving the polyaldehyde in THF and then adding a significant amount of ethanol to the solution before addition of the $NaBH_4$ (500 mL of THF/70 mL of EtOH). It was found that the proton source helped to complete the borohydride reduction and prevented hydroxy groups on the polymer from complexing with the borate anions to form an extended cross-linked ionomer. Cross-linking was further prevented by quenching the reduction with 1 M HCl in ethanol. The acid served a dual purpose of quenching any remaining $NaBH_4$ and preventing the newly formed hydroxymethyl groups from complexing to the borate anions in solution.



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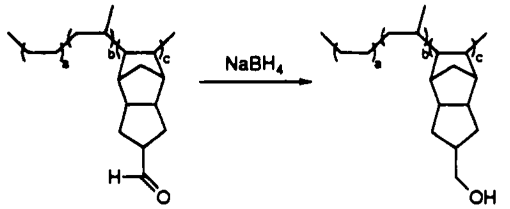

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2. Catalytic Methods

In 1986, Mohammadi, Ling, and Rempel[30] reported a two-step procedure for the hydroxymethylation of polybutadienes using homogeneous rhodium catalysts to hydroformylate up to 20% of the available double bonds in polybutadienes polymers and the formylated intermediates were then hydrogenated with homogeneous ruthenium catalyst which reduced the formyl groups to hydroxymethyl groups and saturated the remaining double bonds (see eq 7). Polybutadienes with a mixture of *cis*/*trans*-1,4- and 1,2-double bonds were hydroformylated in toluene at 60 °C with 1:1 H_2/CO using $HRh(CO)(PPh_3)_3$. The hydroformylated polybutadiene was then hydrogenated using $HRu(CO)Cl(PPh_3)_3$ with H_2 (615 psia) at 90 °C in toluene. In 1991, this work was extended to include styrene-butadiene copolymers by Sibtain and Rempel.[60]

By choosing either chemical or catalytic reduction methods, unsaturated or saturated hydroxymethylated polymers can be produced using a variety of olefin containing polymer substrates.

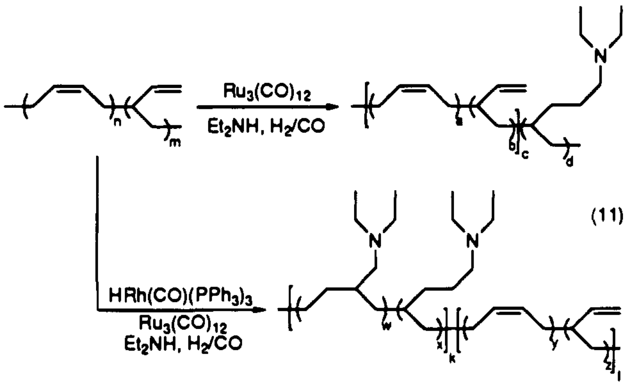
V. Aminomethylation of Olefin Polymers

Early syntheses of amine-containing polymers described the polymerization of amine-functionalized monomers,[63,64,65] the chemical modification of polymers,[66,67] or the reaction of oxidatively degraded hydrocarbon polymers with amine compounds.[68] We have limited our discussion to the post-polymerization, metal-mediated amine functionalization of polymers.

In 1982, Jachimowicz and Raksis[69,70] patented the functionalization of double bond containing polymers by reaction with CO, H_2O, and an amine (a primary amine, a secondary amine, or ammonia) in the presence of a cationic Rh(I) catalyst. For example, 50 parts by weight of polybutadiene ($M_n = 1000$; 80% 1,2-units), 12.8 parts pyrrolidine, 4 parts H_2O, 410 parts *N*-methylpyrrolidine, and 0.25 parts of $[Rh(norbornadiene)\{(CH_3)_2C_6H_5P\}_3]+PF_6$- were loaded into a 1 L reactor. The reactor was pressurized to 1015 psia with carbon monoxide and then heated to 140 °C for 15 h. The final product was approximately 90% functionalized with both aminomethyl and amido groups in equal amounts on the polymer. Water provides the hydrogen source for the process through the water gas shift reaction. Hydrogen added in addition to the water appears to lower the effective yield of the reaction. Under these reaction conditions, primary amines yield tertiary amine groups in the final product and in the case of ammonia as the nitrogen source, secondary amines are formed.

In 1985, Jachimowicz and Hansson[71,72] extended this work to include a number of rhodium, ruthenium, and iridium catalysts. Rhodium catalysts were found to be the most effective but high degrees of functionality could also be obtained by using mixtures of rhodium and ruthenium particularly when rhodium was the minor component and the Ru/Rh ratio was on the order of 10:1 or greater. It was also found that significantly increased levels of amine incorporation with no amide incorporation could be achieved by running the reaction in an anhydrous organic solvent with H_2 instead of water as the hydrogen source. Jachimowicz also reports that polymeric secondary amines could be made by using bulky primary amines, such as isopropylamine, in the aminomethylation reaction. Considerable hydrogenation of the polymer double bonds also accompanies aminomethylation.[72]

In 1985, Knifton[73,74] disclosed a method for aminomethylating the 1,2-butadiene groups in polybutadienes using a ruthenium catalyst and a novel two-phase solvent system. As an example, 7 gm of polybutadiene ($M_n = 2000$; 70% 1,2), 12 mL of diethylamine, 25 mL of hexanes, 10 mL of dimethylformamide (DMF), and 0.1 gm of triruthenium dodecacarbonyl were added to a 300 mL reactor and pressurized to 515 psia with CO/H_2 (1:1). The reaction mixture was heated to 160 °C for 5 h and by ^1H NMR, the product was 27% aminomethylated. This two-phase solvent system allows for an easier purification of the final product; the ruthenium catalyst separates into the DMF layer and the aminomethylated polymer is essentially all in the alkane layer. The alkane/DMF solvent system also exhibits an increase in selectivity for the aminomethylation reaction. Results indicated that there was negligible hydrogenation of double bonds and aminomethylation took place only on 1,2-double bonds. *cis*/*trans*-1,4-Butadiene units did not appear to react. A number of amines could be used in this reaction; however, in the case of ammonia, the product consisted of a light brown rubbery polymeric solid which was insoluble.[74] This would seem to indicate that as in the previous work by Jachimowicz[69] polymeric secondary amines have formed by the use of ammonia and the multiple reactions on the same nitrogen needed to form secondary amines has led to a cross-linked, insoluble material.



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In 1987, McEntire and Knifton[75] patented an improvement upon the two-phase aminomethylation chemistry which allowed for the aminomethylation of *cis*/*trans*-1,4 as well as 1,2-double bonds on polybutadienes. McEntire and Knifton found that by using a mixture of rhodium and ruthenium catalysts, such as $HRh(CO)(PPh_3)_3$ and $Ru_3(CO)_{12}$, and a sterically hindered phosphine, such as tris(*o*-methoxyphenyl)phosphine, as the catalyst system and running the reaction at higher pressures, 1015–4015 psia, with a 2:1 H_2/CO mixture, *cis*/*trans*-1,4-butadiene units as well as 1,2-butadiene units would be aminomethylated.

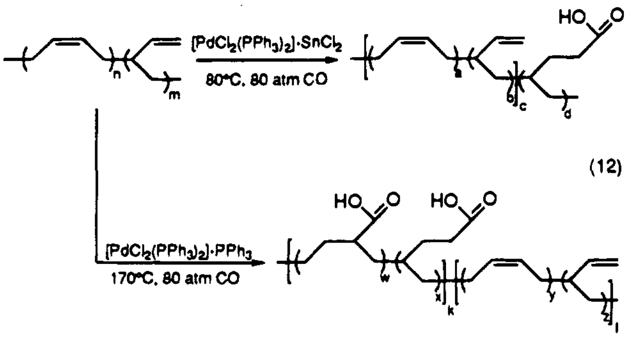
In 1992, Wideman,[76] patented a method for aminomethylating olefin containing polymers with paraphenylenediamine groups to make polymeric antidegradents for sulfur vulcanizable rubbers. Polybutadiene comprised of 65% 1,2-butadiene units was hydroformylated using $Co_2(CO)_8$ at 215 psia of H_2/CO (1:1) at 100 °C for 50 min in the presence of a primary or secondary amine paraphenylene diamine antidegradent, such as 4-aminodiphenylamine. The reaction was typically run until 1–2% of the double bonds had been functionalized with paraphenylenediamine groups. Permanent attachment of the amine functionality was determined by washing the material with acetone and then observing infrared absorption bands corresponding to polyenamine and polyamine groups in the dried polymer. No other analysis is mentioned.

VI. Hydrocarboxylations

The reaction of interest involves the reaction of the template polymer with carbon monoxide and either water or an alcohol in the presence of a catalyst in order to produce a carboxylated polymer. Polycarboxylic acids are typically prepared by polymerization of acid-functionalized olefins such as acrylic acid or maleic anhydrides.[77] These polymers all have the carboxy function directly attached to the main chain of the polymer. Carboxylic acids can also be grafted to polymer chains by either radical or thermal reactions (ene reaction).[78] Anionic modification of polybutadienes and polystyrenes has been demonstrated with alkyllithiums and carbon dioxide.[79]

Polycarboxylic acids via catalytic hydrocarboxylation of polybutadienes offers a way of attaching carboxylic acid groups at the terminal olefin sites.[80] A process for the production of carboxylic acid functionalized polymers that utilizes the residual carbon–carbon bonds of polyisobutene has also been patented.[81]

Recently the hydrocarboxylation of a wide variety of different polybutadienes has been thoroughly studied and it was found that different catalyst systems can lead to different selectivities.[82] By using $[PdCl_2(PPh_3)_2]-SnCl_2$ as a catalyst, the carboxylic acids are placed predominantly at the 1,2-positions.[82] The functionalization reaction is usually carried out at 80 °C, 1176 psia CO for 4 h in methyl isobutyl ketone. When the reaction is performed with $[PdCl_2(PPh_3)_2]-PPh_3$ in benzene at 1176 psia CO at 170 °C or with $PdCl_2-CuCl_2-O_2$ (7.3 psia in THF at 25 °C for 24h) both 1,4- and 1,2-carboxylated polymers are formed.[82]



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The research of Cole-Hamilton and co-workers[82,83] demonstrates the most selective use of catalyst system to control functionalization at either the backbone or terminal positions. The extent of functionalization for these systems is usually high, but there is no mention of attempts to control functional density.

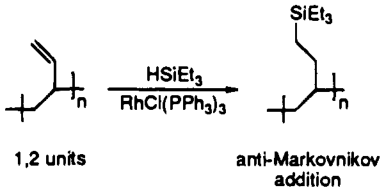
Polybutadienes and butadiene-styrene copolymers have been hydroesterified with cobalt catalyst/pyridine, CO (765 psia), and an alcohol at 150 °C.[84] This reaction does not appear to be that selective since it produces cyclic ketones and saturated and unsaturated carboxylic esters.

VII. Hydrosilylation of Olefin Polymers

The addition of the Si–H bond to carbon–carbon double bonds of polymers offers a useful method of preparing silane-modified polymers.[85] Although there are numerous examples[85–104] of the use of hydrosilylated polymers as components of polymer systems there is little mechanistic and quantitative information about this modification procedure. Recently the details of both the platinum- and rhodium-catalyzed hydrosilylation reaction with various polybutadiene and copolymers of polybutadiene has been studied.

A. Rhodium-Based Catalysts

The hydrosilylation of polybutadiene catalyzed by $Rh(PPh_3)_3Cl$ was studied by Rempel.[105] The addition of trialkylsilane groups to a $M_n = 4500$ polybutadiene (P(bd)) occurs at the 1,2-butadiene units. Furthermore the trialkylsilane can add the SiH at the 1,2-units in either an anti-Markovnikov addition resulting in the Si being attached at the terminal position or the Markovnikov addition resulting in the Si being placed at the iso position of the 1,2-unit. Rempel *et al.*[105] found that the reaction of a toluene solution of 45% 1,2-butadiene units P(bd) (M_n = 4500) at 110 °C with triethylsilane and Wilkinson's catalyst resulted in hydrosilylating 43% of the butadiene units (by ^1H NMR). After a 1.5 h induction period, 30% conversion occurred in 1.5 h and a 43% conversion after 10 h. Further addition of triethylsilane did not increase the degree of hydrosilylation. Similar results occurred with tributylsilane achieving a 45% conversion in 10 h. There appears to be a good correlation in the 1,2-content of P(bd) and degree of hydrosilylation (eq 13).



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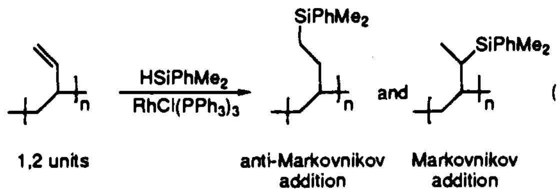
By studying hydrosilylation by ^{13}C, ^1H, and ^{29}Si NMR, information about the selectivity of this reaction can be obtained. ^{13}C NMR suggests that the hydrosilylation of 4500 M_n P(bd) occurs regioselectively via an anti-Markovnikov product resulting with the Si group being attached at the terminal position of the 1,2-P(bd) unit. ^{29}Si NMR further supports the regioselectivity of this reaction with only one detectable ^{29}Si resonance at −1.5 ppm.

These results are consistent with the hydrosilylation studies of monomeric olefins. 1-Pentene hydrosilylates much faster than 2-pentene and no hydrosilylation of cyclohexene was observed. There seems to be a higher regioselectivity with P(bd) when compared to the hydrosilylation of 1-hexene where only 60% of the anti-Markovnikov product is obtained. Rempel[105] speculates that the higher selectivity with P(bd) is due the presence of the bulky polymer chain. Hydrosilylation of P(bd) with dimethylphenylsilane resulted in 43% of the butadiene units being hydrosilylated but with both the Markovnikov (^{29}Si = −2.5 ppm) and anti-Markovnikov (^{29}Si = −12.05 ppm) products being formed (eq 14).



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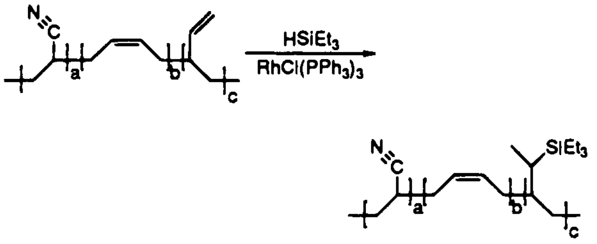
The chain length properties of the hydrosilylated polymers was also examined using vapor phase osmometry and gel permeation chromatography. It was concluded that little change in large-scale molecular structure (compared to the base polymer) occurred during these hydrosilylation reactions.

Rempel *et al.*[106] also studied the influence of the functional groups of copolymers of styrene-butadiene (SBR) and nitrile-butadiene (NBR) on the hydrosilylation reaction. It was found that the reaction mechanism was markedly influenced by the nature of the functional groups in the polymer chain. In the case of SBR the reaction occurred via a typical anti-Markovnikov addition leading to the linear adduct. However when electron-withdrawing groups such as nitriles were present (NBR) the addition appeared to occur via Markovnikov addition mechanism which led to a branched adduct (eq 15). Both NBR and SBR copolymers appear to be selective toward 1,2-butadiene unit hydrosilylation.



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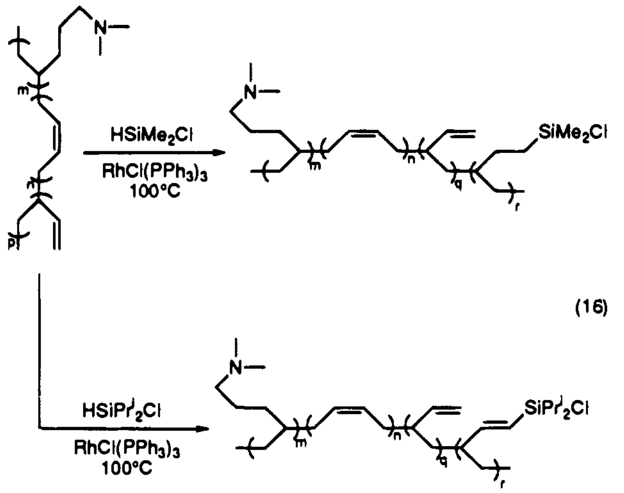
The hydrosilylation of an aminomethylated P(bd) with chloroalkylsilanes and Wilkinson's catalyst was studied by Tremont *et al.*[1] and a change of mechanism was observed when bulkier chlorosilanes were used. The reaction of aminomethylated P(bd) with dimethylchlorosilane resulted in the expected anti-Markovnikov product. When the same reaction was performed with diisopropylchlorosilane, the vinyldiisopropylsilane product was formed. The attachment site was characterized by NMR spectroscopy after the silyl chloride functionalized polymer was converted to the methoxy derivative with methanol. Proton−silicon and proton−carbon indirect detection experiments (HMQC, HMBC) gave strong evidence for the identity of the attached functional groups. The ^{29}Si chemical shift for the vinyldiisopropylsilane product was 6.5 ppm. Evidence was seen for long-range bonding relationships between the silicon and (1) the diisopropyl protons (0.9−1.0 ppm), (2) methoxy protons (3.4−3.6 ppm), and (3) olefinic protons (5.4 and 5.8−5.9 ppm). One of the olefinic protons exhibits a proton−carbon correlation peak at 5.8−5.9 ppm (^{1}H) and 154−155 ppm (^{13}C). No evidence was seen for a saturated methylene linkage to the silicon in either the proton−silicon or the proton−carbon indirect detection experiments. With the diisopropyl and methoxy groups accounting for three of the four possible binding sites to the silicon, the olefinic correlations represent an unsaturated linkage to the polymer. These results indicate the steric constraints placed on both the polymer and the silane can change the mechanism of the hydrosilylation reaction.



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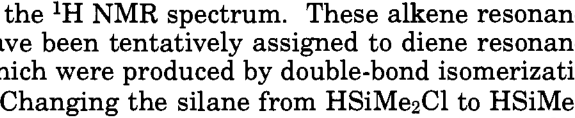
B. Platinum-Based Catalysts

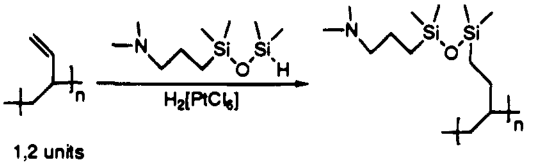
Besides the Rh-catalyzed hydrosilylation reaction of P(bd), the Pt-catalyzed[85−104,107] hydrosilylation has been extensively used to produce silyl functionalized polymers. Until recently little detail about the Pt-catalyzed reaction was known. A detailed study of the hydrosilylation reaction of polybutadienes catalyzed by $H_2[PtCl_6]$ was studied by Cole-Hamilton *et al.*[108] Polybutadienes of various microstructures were hydrosilylated with $HSiMe_xCl_{3-x}$ in toluene at 80 °C using $H_2[PtCl_6]$ as the catalyst. With all $HSiMe_xCl_{3-x}$ (x = 0 to 2) complete functionalization of the 1,2-double bonds occurs with Me_2SiHCl being introduced selectively onto the terminal 1,2-vinyl groups of the polymer. Interestingly the Pt-catalyzed reaction, unlike the Rh system, produced low conversions of some of the internal 1,4-P(bd) units. This is particularly obvious in the reaction of the M_n = 250000 P(bd) which contains >98% *cis* backbone double bonds and for which 27% hydrosilylation occurs (eq 17). In all cases where backbone hydrosilylation occurs, there are new multiplet resonances in the alkene region of the ^{1}H NMR spectrum. These alkene resonances have been tentatively assigned to diene resonances which were produced by double-bond isomerization.



(17)

Changing the silane from $HSiMe_2Cl$ to $HSiMeCl_2$ or $HSiCl_3$ does not alter the efficiency of the hydrosilylation of the terminal double bonds but the reactivity toward the backbone decreases as the number of chlorine atoms on the silicon increases.

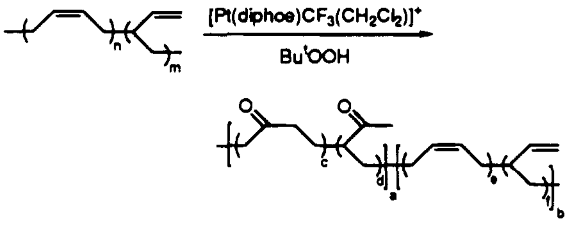
Hydrosilylation catalyzed by hexachloroplatinic acid was also used to attach tertiary amine groups to a polybutadiene polymer. Sauvet *et al.*[109] hydrosilylated polybutadiene with [(3-*N*,*N*-dimethylamino)-propyl]tetramethyldisiloxane in order to graft tertiary amine groups on P(bd) (eq 18). At low silane concentration, the reaction is first order in Pt, second order in silane, and zero order in vinylic double bonds. An inhibitory effect of the aminosilane was observed. At high silane concentration, very sharp acceleration periods are observed which was interpreted as a change of catalyst from a weakly active Pt(II) to as more active Pt(0) catalyst.



(18)

VIII. Oxidation

Oxidation of the double bonds in polybutadienes to produce polyketones has been reported by Iraqi and Cole-Hamilton.[110] Polybutadienes of various microstructures were reacted with *t*-BuOOH in the presence of $[Pt(Ph_2PCH{=}CHPPh_2)CF_3(CH_2Cl_2)]^+$ (eq 19). Conversions as high as 57% are reported. From the ^{13}C NMR analysis of the products, the reactivity ratios of the different types of double bonds present in polybutadienes appears to be 6:5:3 for 1,2/*trans*-1,4/*cis*-1,4. In a later communication,[111] Iraqi also reports that polyketones made by the method outlined above could also be further modified by reacting with 6-lithio-2,2′-bipyridyl to functionalize polybutadienes with bipyridyl groups.



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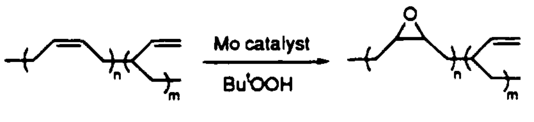
IX. Epoxidation

Popova *et al.*[112] reported the epoxidation of butadiene and 1,3-pentadiene rubbers using *t*-BuOOH and $MoO_2(acac)_2$ as a catalyst at 115 °C. *cis*-1,4-butadiene and *cis*-1,4-pentadiene units were found to react 2.2–3 times faster than their *trans* counterparts and total conversions reached 68–92%.

Gahagan *et al.*[113] have reported a very highly selective catalyst system for the epoxidation of polybutadiene. Using MoO_2Cl_2[3-(diethoxyphosphinyl)-camphor] as a catalyst and *t*-BuOOH as the oxidant, all of the *cis*/*trans*-1,4-double bonds of polybutadiene were epoxidized while the 1,2-double bonds remain unreacted. It is surprising that such high selectivities should be exhibited for polybutadiene when under the same conditions small molecule terminal olefins, such as 3-methylbut-1-ene and 3,3-dimethylbut-1-ene are epoxidized to at least 25% conversion.[113]



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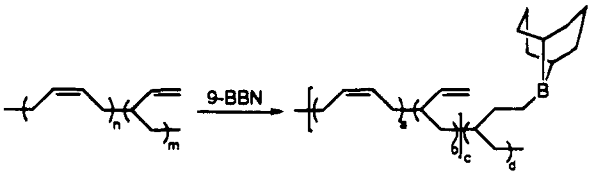
X. Hydroboration

While not strictly a metal-mediated process, hydroboration of olefin containing polymers has been used by several groups for the controlled functionalization of polymeric backbones. The method used for successfully placing controlled amounts of functionality on a polymer backbone using hydroboration was first described by Chung *et al.*[114] Olefin-containing polymers, such as 1,2-polybutadiene, 1,4-polybutadiene, and polyisoprene, were hydroborated with a dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN), under vacuum and at low temperatures, −10 °C (eq 21). The amount of boration could be controlled by the amount of the borane charge. A completely oxygen-free atmosphere was maintained to prevent gelation of the trialkylborane intermediate. The hydroborated polymer was then further modified by oxidizing the borane groups with $NaOH/H_2O_2$ to produce polyols. The oxidation step was also performed under vacuum and at low temperatures, −25 °C, to prevent polymer gelation. It was found that 1,2-polybutadiene, 1,4-polybutadiene, and polyisoprene reacted with 9-BBN with relative reactivity ratios of 1:0.167:0.125, indicating that the steric hindrance about the olefin greatly affected the reaction rate. This sequence of hydroboration and oxidation was used to produce polyols with 30% functionality and 100% functionality.

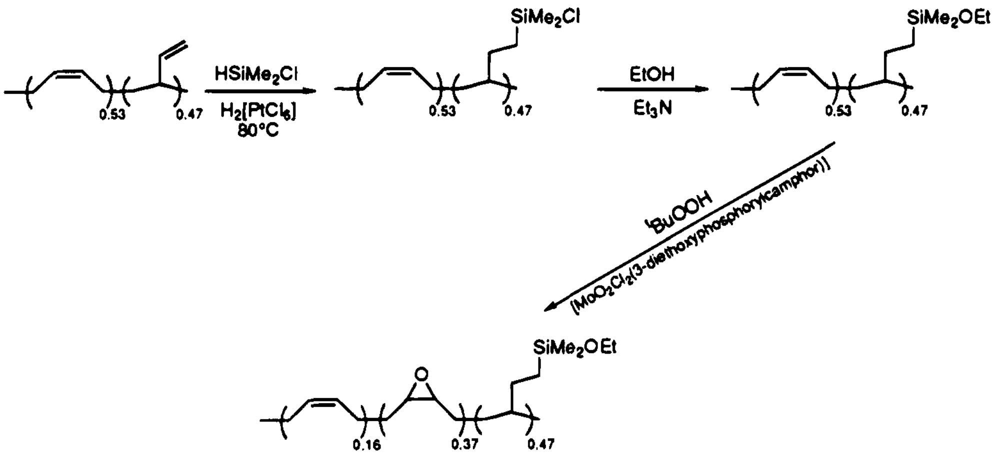


(21)

This same chemistry was used by Adams and Gronski[115] to prepare polymers with liquid crystalline side chains. A copolymer of styrene and butadiene was hydroborated with 9-BBN, which reacted selectively with the butadiene units. The borane groups were oxidized with $NaOH/H_2O_2$, generating a copolymer functionalized with hydroxyl groups. The hydroxyl groups were then used to attach the liquid crystal mesogen, 2-cholesteroloxycarbonyl, to the polymer backbone. By using the very selective hydroboration reaction, Adams and Gronski[115] were able to start with a copolymer of known molecular weight and attach liquid crystalline groups to the polymer backbone without significantly affecting the molecular weight distribution.

Hydroboration of olefin-containing polymers has also been used to study the effects of polymer microstructure on physical properties. Ramakrishnan[116] reported the hydroboration and oxidation of olefin-containing polymers made by the ring-opening metathesis polymerization (ROMP) of various cyclic

Scheme 1. Synthesis of Difunctional Polymeric Adhesive



olefins. The techniques for hydroboration and oxidation were the same ones reported by Chung *et al.*[114] The polyols formed by the hydroboration and oxidation of these polyalkylenes were analogous to commercial polymers made by the copolymerization of ethylene and vinyl alcohol; however, commercially made ethylene-vinyl alcohol copolymers often contain a certain amount of branching while the polymers made by the ROMP–hydroboration–oxidation sequence do not contain any branch points and have well-defined microstructures controlled by the reactants and reaction sequence. By using a variety of cyclic olefins as starting materials, Ramakrishnan was able to investigate the physical properties of a series of polymers with well controlled changes in microstructure and hydroxyl content.

XI. Design of Multifunctional Polymers by Sequential Catalytic Reactions

One of the exciting uses of catalytic reactions on polymers involves sequential catalytic reactions of a base polymer such as polybutadiene in order to fine-tune the properties of the specialized polymer system. This methodology has been used to prepare a novel dual functional adhesive,[108] polymer-bound metals systems, polyols,[111] and tailor-made delivery systems for prostaglandins.[1]

A. Polymer Adhesives

Cole-Hamilton *et al.*[108] were interested in sequentially introducing two different functional groups on the same polymer in order to produce specialty films that have the potential of improving the adhesion of metal oxide films to surfaces. The goal of this research was to selectively incorporate epoxides into the backbone and a trimethoxysilyl group onto the pendant double bonds. It was found that the target difunctional polymer could be obtained by first hydrosilylating a P(bd) containing 47% 1,2-butadiene groups with chlorodimethylsilane to produce a silylated polymer in which 47% of the butadiene units (all of the 1,2-units) have been hydrosilylated. The chlorosilane polymer is then converted to the ethoxydimethylsilyl functionalized P(bd) by reaction with ethanol and triethylamine in order to prepare a less reactive polymer. Next, the silylated polymer is epoxidized with *tert*-butyl hydrogen peroxide and MoO_2Cl_2[3-(diethoxyphosphinyl)camphor]; this procedure epoxidizes 70% of the available internal 1,4-butadiene units. This polymer has alkoxysilane groups and epoxide groups separated by five-atom spacers and has the potential of improving the adhesion of metal oxide films to surfaces (Scheme 1).

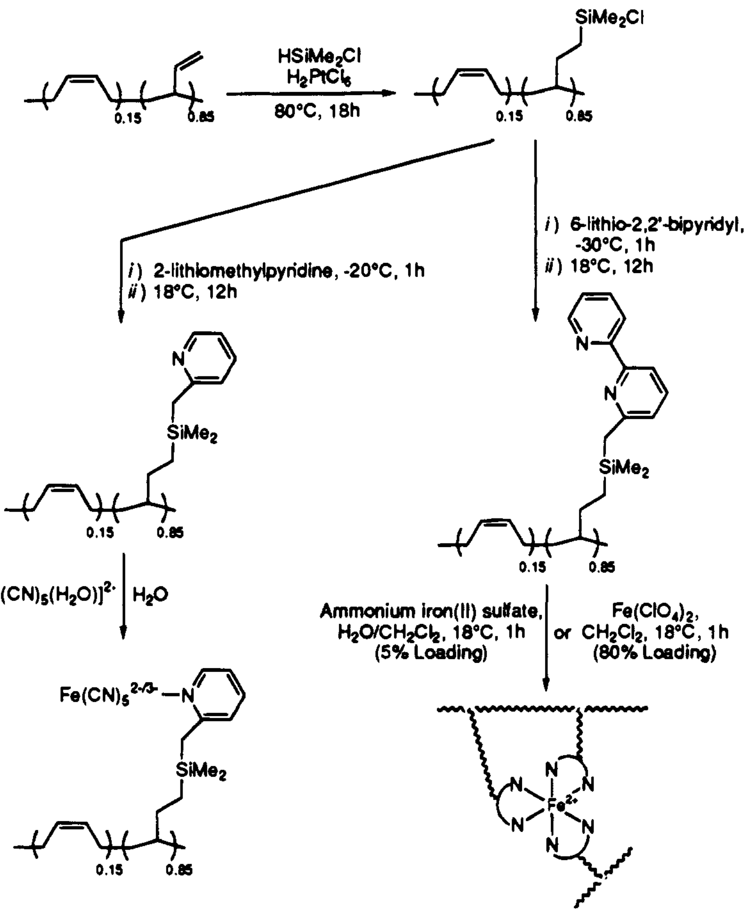
B. Polyols via Catalytic Hydroformylation and Hydroxymethylation Reactions

By sequential catalytic hydroformylation and hydrogenation chemistry, styrene-butadiene copolymers can be readily transformed into hydroxymethylated polymers at various degrees of conversion.[60] Various types of a styrene-butadiene copolymers (SBR rubbers) can be hydroformylated under ambient conditions with $HRh(CO)(PPh_3)_3$. The degree of conversion can be easily controlled using an automated gas consumption apparatus. The hydroformylated SBR-copolymer can then be hydrogenated with $HRuCl(CO)(PPh_3)_3$ to produce the hydroxymethylated polymer in which all of the remaining butadiene bonds have been saturated. The transformations were characterized by infrared and ^{13}C and ^{1}H NMR spectroscopy.

C. Polymer-Bound Ligands and Metal Complexes

There is a considerable interest in the binding of metal complexes to polymers because of their potential electrochemical, photochemical, or conductive properties.[111] Polybutadiene can be hydrosilylated using H_2PtCl_6 to attach terminal dimethylchlorosilane groups. The chlorosilyl functionalized polymer smoothly reacts with 2-(lithiomethyl)pyridine and 6-lithio-2,2′-bipyridyl to give organic-soluble polymer-bound pyridine or bipyridyl functions respectively[111] (Scheme 2). These polymer-bound ligands react readily with metal to form polymeric metal complexes. For example, the bipyridyl containing polymer reacts readily with aqueous ammonium iron sulfate to produce a red polymer which is soluble in chloroform. Atomic absorption analysis indicates that about 5% of the bipyridyl groups are bound to the polymer and UV–vis studies show that each iron atom is surrounded by three bipyridyl ligands. Electrochemical studies in water of the polymer with 5%

Scheme 2. Synthesis of Polymer-Bound Ligands and Metal Complexes



loading of Fe^{2+} cast as a film from methylene chloride onto an indium tin oxide electrode show a clear response from a surface immobilized Fe^{III}/Fe^{II} couple at $E^0 = 0.86$ V.

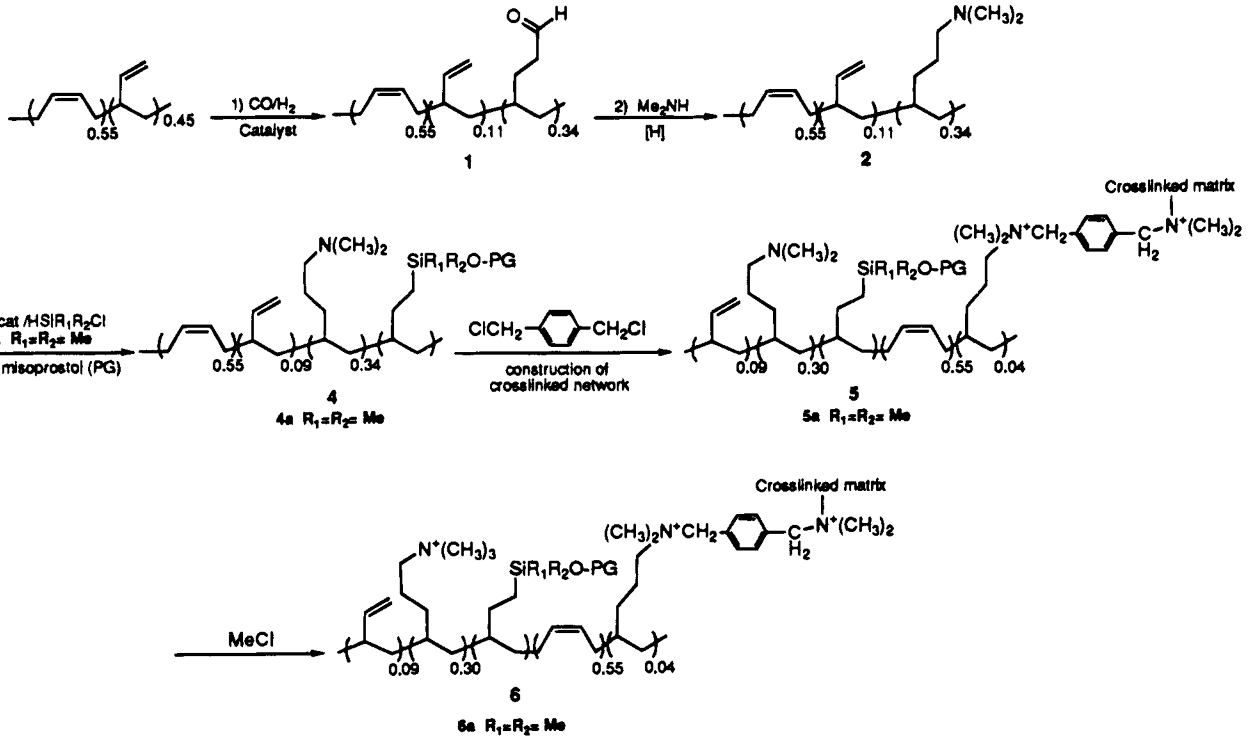
D. Tailored Drug Delivery Systems for Prostaglandins

Sequential catalytic functionalization of polymers offers a new method to build a tunable, tailored system for delivery of drugs. This methodology was used by Tremont *et al.*[1] to tailor a system to deliver the prostaglandin, misoprostol, selectively to the stomach. By use of homogeneous catalysis, functional groups are added to a base polymer to serve a variety of purposes. Organosilyl groups are used to covalently attach the active drug to the polymer and to selectively release the drug in the stomach at an adjustable rate. In particular, this research examines the usefulness of silyl ether functional groups in selectively delivering a drug to the stomach at a controllable and adjustable hydrolysis rate. Other functional groups are also employed to fine-tune the hydrophilicity of the polymer matrix and to create a pH dependent mechanical gate for opening the polymer.[117,118]

Utilizing catalytic reactions on commercially available P(bd) that contains 45% 1,2-butadiene and 55% 1,4-butadiene, the delivery system (Scheme 3) was constructed in a six-step synthesis. The steps were (1) controlled addition of hydrophilic groups by hydroformylation of polybutadiene using hydridocarbonyltris(triphenylphosphine)rhodium with excess triphenylphosphine as the catalyst and (2) reductive amination of the polyaldehyde to the polyamine with ruthenium carbonyl; (3) attachment of the pH-sensitive linker by hydrosilylation of the polyamine with either tris(triphenylphosphine)rhodium chloride or platinum divinyl tetramethyldisiloxane complex; (4) formation of the pH sensitive silyl ether drug bond by coupling of misoprostol to the silyl chloride polymer; (5) construction of an interconnected network by cross-linking of the misoprostol-polymer via the amine functional groups; (6) methylation of the cross-linked polyamine.

The release of the prostaglandin is controlled by acid hydrolysis in the stomach of the silyl ether drug bond. The release rate properties of the polymer matrix were fine-tuned by extending the hydrosilylation reaction to bulkier chlorosilanes. An analog study in which the R groups on the organosilyl linker were changed determined that the diisopropylsilyl linker produced the polymer system with the optimal drug release rate. This study in which only one polymer variable was changed could easily be accomplished by catalytic reactions of P(bd). As stated above in the hydrosilylation section, the silylation of the 1,2-butadiene groups of polyamine **2** with dimethylchlorosilane produced the expected saturated polymer−Si bond ($-CH_2CH_2Si(CH_3)_2Cl$). Interestingly, the silylation of **2** with diisopropylchlorosilane produced either a saturated polymer−Si bond when platinum divinyl tetramethyldisiloxane was used as a catalyst or an unsaturated polymer−Si bond

Scheme 3. Synthesis of Polymeric Delivery Systems



(—CH=CHSi(i-Pr)$_2$Cl) when Wilkinson catalyst was employed.

This study demonstrates that metal-catalyzed reactions on a template polymer can be used to design tailored drug delivery systems. This study also demonstrates the usefulness of an organosilyl prostaglandin linker in achieving a selective stomach-directed delivery system. The pharmacological properties of these delivery systems confirmed the theory that controlled release of misoprostol at its site of action provides effective antiulcer activity while reducing or eliminating systematic and intestinal side effects.[1]

XII. Special Considerations for Chemical Reactions on Polymer Chains

The modifications of polymers by reaction with low molecular weight reagents in solution (so-called *polymer analogous* reactions) present a variety of special issues generally related to the statistics and kinetics of the reactions and products on the polymer chain.[119] These issues offer important insight into the scope and limitations of what might be achieved by a given reaction on a polymer. For example, it is well known that the products of polymer analogous reactions possess a "compositional heterogeneity",[119] *i.e.* a population of chains whose individual conversion levels vary about the average value, and that this phenomenon is a function of both the extent of reaction and the particular set of chain lengths in the substrate polymer population. Forster *et al.*[45] considered this heterogeneity when preparing polyols of low target conversion in order to minimize the number of nonreacted and singly reacted chains in their product. Another example is a potential neighboring group effect on reaction kinetics, which will have implications for the reaction times needed to achieve a given conversion, possible upper limits to conversion (of which there are several examples in the work reviewed here), and general "blocky" or "alternating" character of the reacted and unreacted site distribution up and down the polymer chains. Similarly, solvent effects can be strongly manifested in reaction rates, conversion limits, and site distributions.

It appears that, with one exception,[58,59] such issues as these have not been studied in detail for metal-mediated chemistries. A framework does exist from non-metal-mediated polymer chemistry, however, and in this section we highlight pertinent aspects of this framework. Notable reviews in this area, including various inter- and intramolecular reactions, have been published by Boucher,[120] Platé and Noah,[119] and Soutif and Brosse.[121] The extensive contributions of Boucher,[122–125] Platé and Litmanovich and co-workers,[126–128] and Gonzalez and co-workers[129–133] represent fundamental developments of the mathematical descriptions of the kinetics of polymer analogous reactions. The work of Gonzalez and co-workers includes extensions to copolymers. Evans considers many of the issues in the broader context of the statistics of filling one dimensional lattices.[134–138] Entelis et al.[139] discuss various methods of determining functionality of functional polymers.

Perhaps the most distinctive of the polymer specific issues is the previously mentioned fact that the product material will have chain-to-chain variations in both the number of reacted sites present and the manner in which the site are distributed up and down each chain. This is a consequence of the "localization" of the reactions and products on the polymer chain, with two effects. First, at any time the state of each chain reflects the accumulation of its particular experience in the natural statistical fluctuations present in the reaction (such as molecular collisions). Second, the reactivity of any particular site on a chain is rendered a function of a microenvironment influenced by[119] (a) neighboring groups, (b) local concentrations, (c) chain conformation, and (d) association or aggregation of chains. In the case of metal-mediated chemistry we need also to add (e) special interactions of catalyst with chains.

These are difficult issues, and the bulk of analyses are thus focused on the more approachable question of the near-neighbor influence (cooperativity) on the kinetics and statistics of polymer analogous reactions.[122,124,125,140-150] The kinetic analyses are generally cast in the form of distributed rate constant models, in which the reactivity of an active site on a polymer chain is considered to be a function of the "unreacted" or "already reacted" state of its near neighbors. Most models consider only nearest neighbors, immediately to the right or left of the site in question, and hence feature "cooperativity of range 1". Although nomenclature varies, the models generally consider three rate constants, say k_0, k_1, and k_2, that dictate the reactivity of a site depending on whether 0, 1, or both of its neighbors have already reacted.

There are three basic reaction classes apparent in this approach. Cases in which $k_0 > k_1 > k_2$ are called autoretarding reactions. These will slow down as the reaction proceeds, particularly beyond 50% functionalization, and produce polymers with "highly alternating" functionality and lower compositional heterogeneity.[151] Cases for which $k_0 < k_1 < k_2$ are autocatalytic. These reactions show accelerated rates at high conversion and produce polymers with "lumpy" or highly associated functionality and possibly high compositional heterogeneity.[126,151] It has been postulated[126] that it is the acceleration by the *first* near neighbor that is most important for autocatalytic reactions. Finally, cases for which $k_0 = k_1 = k_2$ exhibit first-order kinetic behavior and produce polymers with a completely random (often called Bernoullian) distribution of functional sites. For all of the kinetic cases, compositional heterogeneity goes through a maximum at ca. 50% conversion, and it decreases with increasing degree of polymerization of the substrate polymer.[126] Kinetic cases of special interest include the completely random reactions, for which the statistical description of the distribution of functionality is straightforward,[119] and the "completely protecting" reactions, in which reacted sites completely block their near neighbors. In this case there will be an upper limit to conversion, which is a piece of information that has been used as a tool in the sequence analysis of copolymers.[129-131]

There are two aspects of the kinetic models that need special mention. First, they generally consider only "ring" polymers or chains of infinite length as a means of avoiding the ambiguities presented by end groups. This is clearly an approximation, but there does not appear to be a systematic study of the errors introduced for nonring polymers of finite chain lengths. It appears that end effects may be significant for polymers with less than 30 to 100 units.[119,125,132] Also, although the kinetic models predict the distribution of *unreacted* sites up and down the chain, except in special cases[126,152] they do not predict the distribution of *reacted sites*. This can be appreciated intuitively by recognizing that there is more than one way to arrange a given number of reacted sites while maintaining the distribution of unreacted sites found explicitly by the rate models. The prediction of *reacted* site distributions requires further assumptions regarding the fundamental statistical nature of chain functionalization. A useful example of these approaches is found in the β-approximation of Platé *et al.*[128] for estimating the probabilities of arbitrary sequences of reacted and unreacted sites. Monte Carlo simulation has also been used extensively to study site distributions as well as compositional heterogeneity.[126,127,153,154]

Finally, it is noted that special interactions of the catalyst with the polymer chain can be manifested in at least two ways. First, catalysts with a high affinity for the functional groups on the polymer may be difficult to remove from the product. It is thus useful to consider reaction conditions that minimize catalyst usage or to search for efficient antisolvents for polymer washing. Second, there is the obvious concern that the action of the catalyst may be somehow restricted or localized to one section of the catalyst chain. Although there is little published in this regard, it may be considered in the general case by comparing the "time scale of a diffusive event" [155] to the reaction rate of the catalyst. It will be found that over a wide range of conditions the diffusion rate of the catalyst is several orders of magnitude faster than the catalyst turnover rate. When this is true, a catalyst with unrestricted mobility should thus have plenty of time to move among the polymer's sites between reactive events and yield products with functional site distributions and kinetics approaching those determined by the statistical models.

Although the preceding issues can be complex and cannot always be controlled, they can manifest themselves in polymer analogous reactions through constrained conversion levels, shifting kinetics, and distributed functionality. There is thus good reason for at least a first pass consideration as an aid in the design of reactions on polymers and in the interpretation of results.

XIII. Conclusions and Perspectives

Functional polymers are useful building blocks for specialty systems. Metal-mediated reactions on unsaturated polymers are one method of transforming base polymers to multifunctional systems with control of molecular weight and functional density of attached groups. This methodology allows the chemist to prepare multifunctional polymers by sequential catalytic reactions on a base polymer. Reactive functional groups can also be placed on a fixed chain length polymer without unwanted cross-linking reactions. As illustrated in this review, these functional polymers offer a new set of building blocks to the construction kit available to the synthetic chemist.

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