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Modification of Polymers

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Volume 21 MODIFICATION OF POLYMERS
Edited by Charles E. Carraher, Jr., and James A. Moore

PREFACE

The sheer volume of topics which could have been included under our general title prompted us to make some rather arbitrary decisions about content. Modification by irradiation is not included because the activity in this area is being treated elsewhere. We have chosen to emphasize chemical routes to modification and have striven to present as balanced a representation of current activity as time and page count permit. Industrial applications, both real and potential, are included. Where appropriate, we have encouraged the contributors to include review material to help provide the reader with adequate context.

The initial chapter is a review from a historical perspective of polymer modification and contains an extensive bibliography. The remainder of the book is divided into four general areas:

Reactions and Preparation of Copolymers
Reactions and Preparation of Block and Graft Copolymers
Modification Through Condensation Reactions
Applications

The chemical modification of homopolymers such as polyvinylchloride, polyethylene, poly(chloroalkylene sulfides), polysulfones, polychloromethylstyrene, polyisobutylene, polysodium acrylate, polyvinyl alcohol, polyvinyl chloroformate, sulfonated polystyrene; block and graft copolymers such as poly(styrene-block-ethylene-co-butylene-block-styrene), poly(1,4-polybutadiene-block ethylene oxide), star chlorine-telechelic polyisobutylene, poly(isobutylene-co-2,3-dimethyl-1,3-butadiene), poly(styrene-co-N-butylmethacrylate); cellulose, dextran and inulin, is described.

A number of divergent applications are described here: modification of polymer surfaces (coatings, fibers, films and plastics); modifications leading to superior coating materials; isolation, concentration and containment of uranium; natural materials for insulation; synthesis of sugar substitutes; synthesis of anti-arrhythmic drugs; fibers which can be spun from chlorinated solvents yet dry cleaned; and synthesis of calcium ion selective electrode materials.

PREFACE

Polymer modification is a broad, rapidly expanding area of science and the enclosed chapters give glimpses of many of the more important areas. The contributors include a mix of eminent industrially and academically based scientists from any countries which give the book an international flavor.

We thank the authors for their valued contributions and Divisions of Organic Coatings and Plastics and Polymer Chemistry for their support. The cooperation of referees is also gratefully acknowledged.

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MODIFICATION OF POLYMERS[1]

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Polymers of natural origin (gums, fibers, skins) have been used by man since prehistoric times. The technology of improving the useful qualities of such materials was developed empirically without benefit of the unifying conceptual framework of chemistry. The early chemical efforts which lead to the modification of rubber via isomerization with acid (1781)[2] or Vulcanization with sulfur (1839)[3] were also largely serendipitous discoveries. By the mid-19th century investigators like Bracconnot (1833)[4] and Schönbein (1845)[5] had begun systematic efforts to apply the emerging science of organic chemistry to the task of modifying the end-use properties of natural materials, or imparting wholly new properties to them. The careful study of the reaction of cellulose with nitric acid ultimately led to Parkes' production of the first semi-synthetic commercial plastic, "Parkesine" (1864)[6]. The chemistry of polyisoprene isolated from a variety of natural sources was also a subject of intense chemical investigation. It had been chlorinated in 1859[7], and was later hydrochlorinated in 1881[8]. Weber (1894)[9] recognized similarities between the Vulcanization process and the insolubilization of rubber by S_2Cl_2. The production of rayon by treatment of alkali-cellulose with CS_2 was patented in 1892[10]. The preparation of practically useful cellulose acetate by partial hydrolysis of the triacetate was patented in 1903[11], although formation of cellulose acetate had first been cited in 1865[12]. The first report of ethers of cellulose as made in 1905[13].

The commercial utility of materials derived from natural sources and modified by controlled chemical reactions prompted the application of such methods to totally synthetic polymeric materials as they were discovered. The first chemical reaction on a totally synthetic polymer is probably the nitration of poly(styrene) in 1845[14]. An approximate chronology of when reactions on the more common olefin polymers may have occurred may be constructed from a list[15] of the dates these polymers were reported in the literature. An important step forward, both for polymer chemistry in general

Poly(vinylidene chloride)[16]	1838
Poly(styrene)[17]	1839
Poly(vinylchloride)[18]	1872
Poly(isoprene)[19]	1879
Poly(methacrylic acid)[20]	1880
Poly(methyl acrylate)[21]	1880
Poly(butadiene)[22]	1911
Poly(vinyl acetate)[23]	1914
Poly(ethylene)[24]	1933

and for polymer modification in particular, was the development by Staudinger[25] of the concept of the polymer analogous reaction. Staudinger considered a polymer analogous reaction to be a transformation of a polymer into a derivative of equivalent molecular weight. By hydrogenating rubber (1922)[26] and poly(styrene) (1928)[27] essentially without chain degradation, he not only gathered evidence for his macromolecular concept, but he also got the effort to modify synthetic materials off to a running start.

The first literature reference to graft copolymers is the recognition by Houtz and Adkins that polymerizing styrene in the presence of preformed poly(styrene) gave a polymer of increased molecular weight, in which the new styrene units were attached to the original poly(styrene) backbone (1933)[28]. Flory later (1937)[29] proposed that branched vinyl polymers could result from chain transfer reactions involving polymer molecules and growing polymer chains. LeBras and Compagnon (1941)[30] described the modification of the properties of rubber when it was present in polymerizing acrylonitrile, but it was Carlin and Shakespeare (1946)[31] who realized that growing polymer chains should undergo chain transfer, not only with polymer molecules composed of the same monomer units, but also with polymer molecules composed of different monomer units. Branched chains should then be formed in which the backbone chain is composed of one kind of monomer and the branch units of another kind. By polymerizing p-chlorostyrene in the presence of poly(methyl acrylate) and examining the solution properties of the product, Carlin was able to verify this principle (1950)[32]. Examples of the use of cationic techniques include the grafting of isobutylene onto chloromethylated poly(styrene) which had been treated with $AlBr_3$ (1956)[33], the grafting of polystyrene initiated by $SnCl_4$ onto

preformed poly(2,6-dimethoxystyrene) (1969)[34], and the grafting of styrene onto lightly (3%) chlorinated poly(ethylene-CO-propylene) under the agency of diethyl aluminum chloride (1974)[35]. Anionic techniques have also found application to the preparation of graft copolymers. Halasa (1972)[36] has metalated poly(1,4-butadiene) to produce an allylic anion from which the polymerization of styrene could be initiated. Less commonly used are graft polymerizations involving coordinative catalysts (Ziegler-Natta). An elegant example of this approach is the work of Greber (1967)[37]. This procedure involves the addition of diethyl aluminum hydride to a backbone polymer containing pendent unsaturation (e.g., polybutadiene containing some 1,2-sequences) to form a macromolecular trialkylaluminum which can be used to alkylate titanium halides. The resulting Ziegler-Natta catalysts are bound to the backbone polymer and can initiate polymerization of α-olefins to form poly(olefin) grafts.

The first examples of semi-synthetic and synthetic polymers functioning as catalysts and/or reagents developed from the early work on ion-exchange resins[38,39]. Water softening was virtually the only industrial use of ion exchange until the development of synthetic organic ion-exchangers by Adams and Holmes[40] (1935),* They showed that the products obtained by the condensation of polyhydric phenols with formaldehyde could be charged with cations, including hydrogen ions, and that these cations would then exchange with those in solution. Holmes predicted and demonstrated[41] that introduction of a sulfonic acid group into such resins should give more strongly acidic, higher capacity resins. A noteable advance in the manufacture of ion-change resins occurred in 1942 when the late D'Alelio[42] prepared a crosslinked polystyrene resin and sulfonated it with fuming sulfuric acid. The successful preparation of strongly basic anion exchange resins was accomplished by McBurney of the Rohm and Haas Co.[43] some years later by chloromethylating crosslinked polystyrene and then treating it with a tertiary amine to produce quaternary ammonium groups. These materials have not only been used as ion-exchangers but also as effective catalysts for a variety of acid- and base-catalyzed processes[44].

In 1949[45] Harold Cassidy of Yale University took the next step from ion-exchange resins as catalysts, to resins which could function as reagents by accepting or donating electrons. He essentially created the field of redox polymers and was quickly joined by the efforts of Manecke in Germany (1953)[46]. While this concept has remained dormant since Cassidy and Kun's book, "Oxidation Reduction Polymers"[47] was published in 1965, it has gained new currency since

*For reasons of space, the chemical modification of wool, cellulose, coal and other natural substances to produce ion-exchange materials will not be treated here.

the development of such highly electrically conducting polymers as partially oxidized polyacetylene[4] and polythiazyl.[48]

The period from 1960 until now has been one of explosive development in the area of modifying polymers so that they may be used as reagents. In some cases, these reagents mimic (and occasionally surpass) the efficacy of enzymes.[49-52] In the same year of Overberger's first paper on poly(vinyl imidazole), Merrified and Letsinger enunciated the concept of "solid phase peptide synthesis".[53,54] Since then two reviews (among others) on "SPPS" have appeared[55,56] and contain in excess of 2,000 references. In addition, at least five books[57,61] have been published which deal, in whole or in part, with this topic. Since 1977, Polymer News[62a] has published a regular feature in each issue by C. U. Pittman entitled, "Polymer Supports in Organic Synthesis" but we have, to this point, been spared the task (as pleasant as it might be) of reading a journal[62b] devoted only to polymer reactions. This gaping lacuna has now been filled with the publication by Elsevier of "Reactive Polymers, Ion Exchangers, Sorbents", as international journal devoted to the science and technology of these topics under the editorship of F. G. Helfferich.

We stopped counting the number of review articles dealing with the topic of this symposium when the number passed 25. In 1980 two books[60,61] dealing with the subset of reactions on polymer supports were published.

In 1964 Fettes[62] edited the first book[63] the purpose of which was "...covering the various types of chemical reactions that have been carried out with diverse polymeric substances". The editor also noted the magnitude of the problem, "To cover in complete detail all of the published information on all of the reactions of all polymers is certainly difficult and probably impossible...". In a description of the utility of solid phase peptide synthesis Merrifield[64] made the prophetic observation: "A gold mine awaits discovery by organic chemists". Scarely ten years later Leznoff rather ruefully noted: "Many gold nuggets have now been mined... and some iron pyrites". We are currently on the crest of what appears to be an ever-increasing wave and we would have to say that the task described by Fettes is <u>certainly</u> impossible.

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