twofold factor. Therefore any calibration curve obtained from high molecular samples will not be linear. The nonlinearity is not due to exclusion limits of the columns, but represents the use of the undegraded, and therefore untrue, molecular weight. Since the degraded molecular weight of 1.9×10^7 g/mol makes the calibration curve linear, it suggests that polystyrenes of molecular weight greater than about 10^7 g/mol degrade under normal conditions.

Consequently, it must be emphasized that the use of GPC for determining molecular weights when there is a high molecular weight tail in the distribution curve may be seriously in error.

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Communications to the Editor

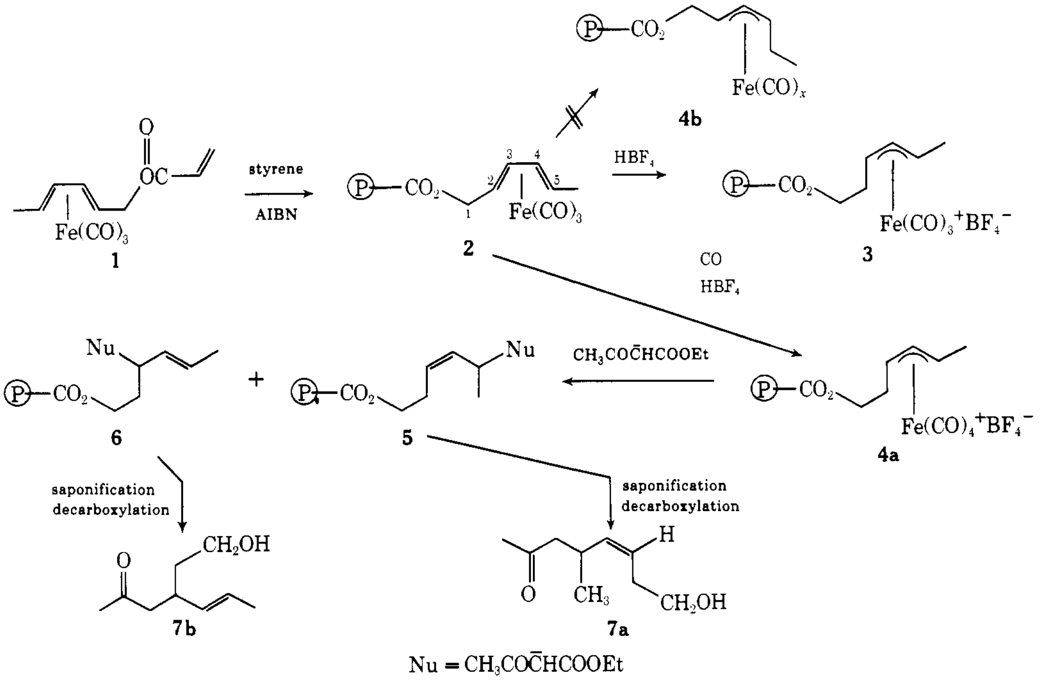
Functionalization of Polymers *via* π-Allyliron Tetracarbonyl Cations

Preliminary studies, reported herein, describe a novel pathway for the functionalization of polymers. We previously reported that η^4-(2,4-hexadienyl acrylate)tricarbonyliron (1) (Scheme I) readily homopolymerized and copolymerized with styrene, methyl acrylate, acrylonitrile, or vinyl acetate.[1] This η^4-(diene)tricarbonyliron function is readily converted in high yield to a polymer-bound π-allyliron tricarbonyl cation, **3**, in the presence of HBF_4[2] or in the presence of both HBF_4 and CO (in CF_3CO_2H) to a polymer-bound π-allyliron tetracarbonyl cation, **4**.[3] The π-allyliron tetracarbonyl cation sites react readily with nucleophiles such as triphenylphosphine or the anion of ethyl acetoacetate to give the 1,4-addition products of the diene moiety.

Protonation of the dieneirontricarbonyl moieties of **2** takes place predominately at C-2 to give **4a** and not **4b**.[4] Treatment of this polysalt with the anion of ethyl acetoacetate gave a mixture of the polymer-bound keto esters **5** and **6**. Their identity was indirectly determined by saponification followed by decarboxylation of the cleaved saponification products to give **7a** and **7b** in a ratio of 4.5 to 1.[5] Thus, predominant attack of the nucleophile on **4a** takes place to give the cis product **5**. In addition to a propensity for cis double bond formation, the nucleophile attacks predominantly at the allyl site farthest from the polymer backbone. This might be a steric effect since both allylic positions are secondary.

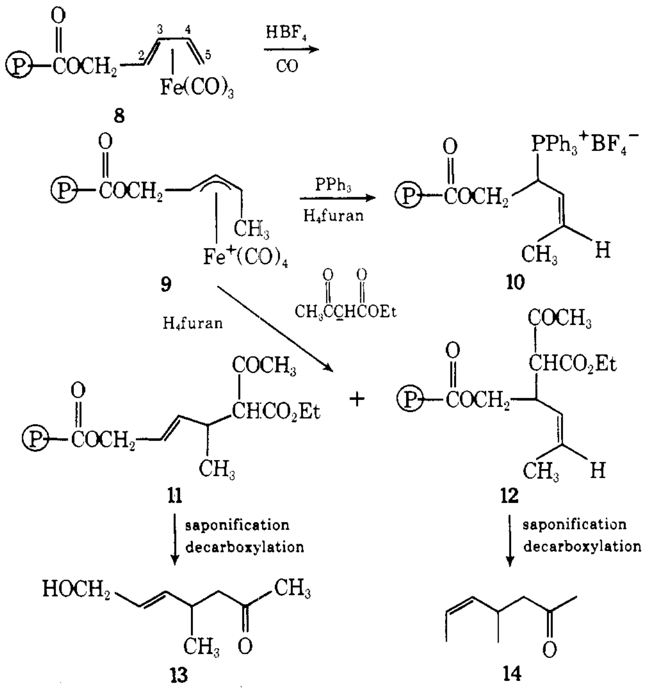
These studies parallel the recent report by Whitesides *et al.*[6] of the specific synthesis of allyl species containing a cis double bond from π-allyliron tetracarbonyl cations. On nucleophilic attack, the cis product was formed even when there is a choice between cis and trans double-bond formation.[6,7] That report prompts our description of simi-

Scheme I



$Nu = CH_3CO\bar{C}HCOOEt$

Scheme II



lar reactions in polymeric π-allyliron tetracarbonyl cations. Copolymers of η^4-(2,4-pentadienyl acrylate)tricarbonyliron and styrene[1] (*i.e.*, **8**) (Scheme II), upon treatment with HBF_4 and CO, gave polysalt **9**, which arises from predominant protonation at C-5. Polysalt **9** could be isolated.[7] Suspension of **9** in H_4furan and addition of the nucleophile resulted in an instantaneous reaction. For example, the addition of excess PPh_3 to **9** gave **10** in which the iron had been completely replaced from the purified poly(phosphonium salt).[8] With the anion of ethyl acetoacetate, nucleophilic attack occurred at both termini of the allylic system resulting in units of both **11** and **12** within the polymer. Saponification and decarboxylation resulted in the isolation of **13** and **14** in a ratio of 7:1 in 53% overall yield.[5,9] Isolation of **13** and **14** confirms that protonation of **8** occurs predominately at C-5,[10] and that nucleophile attack is favored at the allylic site most removed from the polymer backbone.

No evidence was obtained for the presence of intermediate olefin–iron tetracarbonyl complexes after treatment with triphenylphosphine or pyridine. Such complexes, resulting from disubstituted allyl cations, such as **4** or **9**, are very unstable relative to the corresponding complexes derived from the unsubstituted π-allyliron tetracarbonyl cation.[11]

Using this technique it should be possible to convert the η^4-(diene)tricarbonyliron moiety into a variety of pendant functional groups. Since the reactivity ratios are known for the copolymerization of **1** with several organic monomers,[1,12] it is possible to specifically tailor the amount of **1** in copolymers, thereby specifically controlling the number of functional groups to be later introduced *via* the π-allyl cation route.

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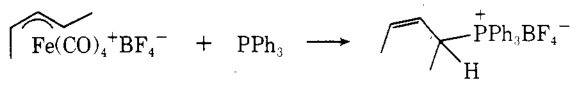
(4) This is inferred based on the products (**7a** and **7b**) which are isolated upon reacting **4** with the anion of ethyl acetoacetate followed by saponification and decarboxylation. Cation **4b** could only lead to *cis*-4-(hydroxymethyl)-5-octen-2-one or *trans*-4-ethyl-5-hepten-7-ol-2-one but not to **7a** or **7b**.

(5) Satisfactory ir, nmr, and mass spectra as well as elemental analyses were obtained for each compound. The cleavage products are readily separated from the polymer backbone by precipitation of the polymer into excess hexane.

(6) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Amer. Chem. Soc.*, **95**, 5792 (1973).

(7) The polymeric salts were precipitated upon adding diethyl ether to the acidic solutions. The starting polymers contained from 3 to 23 mol % of the organometallic monomer.

(8) That a mixture of **10** and Ⓟ-$CO_2CH_2CH{=}CHCH(CH_3)(PPh_3^+)BF_4^-$ was formed has not been ruled out. Compound **10** is presumed to predominate based only on Whitesides[4] observation that the *syn,anti*-(1,3-dimethylallyl)iron tetracarbonyl cation gave rise to a 74% yield of the cis allylphosphonium salt shown.



However, in that case steric effects of the polymer backbone were not present.

(9) Yields were based on the number of η^4-(diene)tricarbonyl units initially present in the polymer and were determined by vpc. Products **13** and **14** were isolated and purified both by liquid chromatography and by preparative vpc.

(10) Predominant protonation at C-2 followed by nucleophilic attack of $CH_3COCHCOOEt$, saponification and decarboxylation would result in the formation of either 3-(2-hydroxyethyl)-5-hexen-2-one or *cis*-5-octen-8-ol-2-one.

(11) For example, Whitesides[4] reported the isolation and characterization of allylpyridiniumiron tetracarbonyl tetrafluoroborate.

(12) Defining **1** as M_1, $r_1 = 0.26$, $r_2 = 1.81$ when styrene is M_2. By adding from 1 to 4% divinylbenzene to copolymerizations of **1** and styrene (where the 1:styrene ratio is 1:6), a crosslinked swellable resin is obtained which can be used for the solid phase synthesis of **7** and **8**. This is analogous to solid support peptide synthesis.[13,14]

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A Chemical Synthesis of Benzylated Methyl α-Isomalto Oligosaccharides

We are engaged in a systematic study of the stepwise synthesis of oligosaccharides. Our work, at present, involves the use of reactive glycosyl leaving groups and a variety of hydroxyl blocking groups in order to achieve rapid completely stereoselective syntheses of glycosides in high yield.[1-6] Recently we have reported that reaction of 2,3,4-tri-*O*-benzyl-6-*O*-(*N*-phenylcarbamoyl)-1-*O*-tosyl-D-glucopyranose (I) with alcohols in diethyl ether gives high yields of pure α-D-glucosides.[6] We now wish to report the stepwise synthesis of methyl octadeca-*O*-benzyl-α-isomaltohexaoside.

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (II; 1 equiv) was allowed to react with I (1.2 equiv) in diethyl ether for 16 hr as previously reported.[5] The product was extracted with dichloromethane, washed with water, and evaporated to a syrup. The syrup was crystallized from di-