Direct Functionalization of Polystyrenes by Platinum(II)-catalyzed Hydroarylation. A New Methodology for Utilization of Polymers

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Direct introduction of an acrylic acid moiety into polystyrenes was first conducted. Reaction of polystyrenes with propiolic acid or its methyl ester in the presence of K_2PtCl_4 and AgOTf afforded alkenylated polystyrenes with up to 35% incorporation of the acrylic acid moiety relative to styrene unit.

Hydrocarbons abundantly exist in nature and most of them are utilized as energy sources for power plants, cars, and our lives. Direct use of hydrocarbons as raw materials for fine chemicals is not commonly conducted since the reactivity of C–H bonds in hydrocarbons is very low because of their strong bond energy. Direct functionalization of the C–H bond in hydrocarbons is a challenging subject in organic synthesis and has been recently studied with great interest.[1] The direct functionalization of hydrocarbons in organic synthesis provides the advantages that no halogenated compounds are required as starting materials and the reaction steps are reduced. Therefore, such processes are also attractive as an environmentally benign synthesis.

On the other hand, polyolefins are ubiquitous commercial polymers and introduction of functional groups into polyolefins is an important tool for development of new polymer materials.[2] Development of a direct and simple procedure for introducing functional groups into polyolefins is strongly desired because functional groups significantly affect or prevent the polymerization of monomers. Especially, not only does introduction of a multiple bond or carboxylic acid into polyolefins lead to a key substituent for converting to new functional groups, but it also provides a significant method for modifying the properties of polymers. Therefore, the development of direct methods for introducing useful functional groups provides an epoch-making methodology for polymer science.

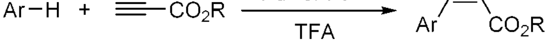
Previously, we have reported that aromatic hydrocarbons react with alkynes in the presence of palladium or platinum catalysts to give arylalkenes, as shown in Scheme 1.[3] This type of hydroarylation of alkynes proceeds under mild conditions to provide various aromatic alkenes and heterocycles. Thus, we examined a direct introduction of an acrylic acid group into polystyrenes by using this hydroarylation tool.[4] However, to the best of our knowledge, there are no reports on such alkenylation of polystyrenes with a direct functionalization method. Here we wish to report a novel functionalization of polystyrenes using the hydroarylation tool.

Although trifluoroacetic acid (TFA) plays a significant role in increasing the reactivity of Pt^{II}-catalyzed hydroarylation of propiolic acid and its esters,[3c–3e] polystyrene is not soluble in TFA. Therefore, we first examined the reaction of a more soluble polystyrene block copolymer containing polyethylene and polybutylene, i.e., polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (**1**).[5] The reaction of polystyrene block copolymer **1** with propiolic acid (**2**) was carried out in the presence of K_2PtCl_4 and AgOTf in TFA and $CHCl_3$ at 60 °C for 24 h. After removal of precipitated metals through a short column of silica gel, alkenylated block copolymer **3** was isolated by precipitation with MeOH followed by filtration. Alkenylated block polymer **3** was analyzed by ^1H NMR and IR spectra. The ^1H NMR did not show any characteristic peaks because of broadness of the peaks. However, the IR spectrum indicated the broad absorption of hydroxy group at 2400–3400 cm^{-1}, the strong absorption of carbonyl group at 1694, 1712, and 1728 cm^{-1} and the medium absorption of double bond at 1631 cm^{-1}, indicating the incorporation of acrylic acid moiety on phenyl rings. Since the same reaction without polystyrene block copolymer **1** did not give any polymers, it was suggested that the acrylic acid moiety was derived from the reaction of **1** with propiolic acid. To obtain further evidence for presence of the acrylic acid moiety, the product polymer was esterified with MeOH using diphenylammonium triflate (Ph_2NH_2OTf) as an acid catalyst, which was developed recently as an excellent acid catalyst for esterification of carboxylic acids.[6] The reaction of alkenylated block copolymer **3** with MeOH in the presence of Ph_2NH_2OTf was conducted in $CHCl_3$ at 80 °C for 24 h. Esterified block copolymer **4** indicated characteristic absorptions of a carbonyl group at 1716 cm^{-1} and of a double bond at 1631 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of esterified block copolymer **4** showed a characteristic peak at 3.81 ppm attributable to the methoxy group. The integration of the methoxy group provided the percentage of the acrylate moiety relative to the phenyl ring.

Equimolar amount of propiolic acid (**2**) relative to the styrene unit with 2% K_2PtCl_4/8%AgOTf did not cause alkenylation but increase in the amount of **2** afforded alkenylated styrene copolymer **3** (Table 1, Entry 2). Further increase in the amount of catalysts and **2** gave the best result leading to 30% alkenylation (Entry 4).[7]

Using the best conditions for hydroarylation of propiolic acid by polystyrene copolymer **1**, we next examined the hydroarylation of methyl propiolate (**5**), in which the expected product would be the same product as alkenylated styrene copolymer **4** observed by the reaction of **2** followed by esterification with MeOH (Scheme 2). Actually, the reaction of polystyrene copolymer **1** with **5** under the same conditions as above gave alkenylated polystyrene copolymer **4** with 35% introduction of methyl acrylate moiety per styrene unit.

Next, the reaction of polystyrene[8] (1 mmol of styrene unit)

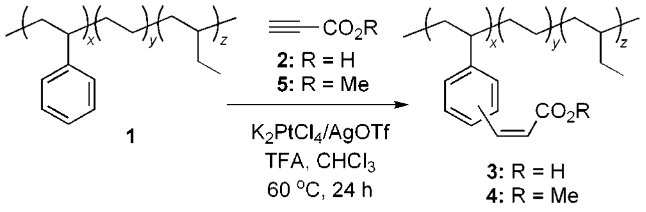


Scheme 1.

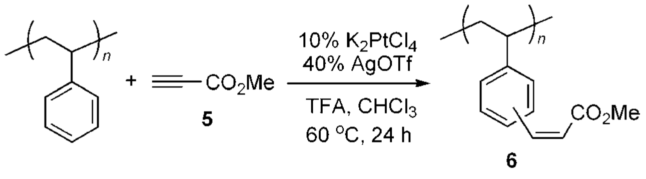
Table 1. Reaction of block copolymer **1** with **2** followed by esterification[a]

Entry	Cat.[b]	**2** /mmol	TFA /mL	$CHCl_3$ /mL	Yield **3**/mg	Alkenylation /%[c]
1	A	1	1	3	332	0
2	A	5	1	3	346	7
3	B	5	2	6	364	11
4	B	10	2	6	336	30

[a] Reaction conditions: **1** (336 mg, 1 mmol styrene unit), **2**, K_2PtCl_4, AgOTf, TFA, and $CHCl_3$ at 60 °C for 24 h. [b] A: K_2PtCl_4 (0.02 mmol), AgOTf (0.08 mmol); B: K_2PtCl_4 (0.1 mmol), AgOTf (0.4 mmol). [c] The percentage of methyl acrylate moiety relative to styrene unit.



Scheme 2.



Scheme 3.

with **2** (10 mmol) was conducted in the presence of K_2PtCl_4 (10%) and AgOTf (40%) in TFA (2 mL) and $CHCl_3$ (4 mL) at 60 °C for 24 h (Scheme 3). The IR spectrum of the obtained product polymer with an almost quantitative recovery (97% by weight) indicated the strong absorption of carbonyl groups at 1696, 1714, and 1729 cm^{-1}, the medium absorption of double bond at 1633 cm^{-1}, and the broad absorption at 2200–3500 cm^{-1}, suggesting the presence of an acrylic acid moiety in the product polymer. The esterification of the product polymer with MeOH in the presence of Ph_2NH_2OTf was conducted in $CHCl_3$ at 80 °C for 24 h. The ^1H NMR spectrum of the esterified polymer showed a characteristic peak assigned to the methoxy group of methyl ester at 3.81 ppm. The esterified polymer indicated the strong absorption of carbonyl group at 1716 cm^{-1} and the medium absorption of double bond at 1634 cm^{-1}. However, the percentage of methyl acryate moiety relative to styrene unit was only 5%. In addition, we examined the reaction of polystyrene with **5** under the same conditions, directly affording polystyrene **6** with methyl acrylate moiety. Analysis of the product polymer **6** by ^1H NMR spectrum showed 7% introduction of methyl acrylate moiety.

The reactions conducted here are considered to proceed with activation of propiolic acid with a platinum catalyst, followed by an electrophilic aromatic substitution on phenyl group of polystyrene or its copolymer.[3e] Although the insolubility of polystyrene in TFA resists direct alkenylation with propiolic acid, introduction of acrylic acid moiety has been achieved by use of K_2PtCl_4/AgOTf catalyst and $CHCl_3$ as a co-solvent.

The utility of acrylic acid moiety consisting of double bond and carboxylic acid as functional groups is considerable high and applicable for functional materials such as photoresists. Therefore, this direct introduction of acrylic acid moiety attracts much attention as a new methodology in materials science. Further development on this subject is now in progress.

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5 Obtained from Aldrich. Copolymer 1 contains 31 wt % of styrene.

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7 Our unpublished result indicated that the hydroarylation of propiolic acid with toluene gave a mixture of ortho and para isomers. Therefore, the alkenylated polymers are considered to be a mixture of ortho- and para-alkenylated polystyrenes. The stereochemistry of the alkene moiety should be almost Z.[3d]

8 Polystyrene (M_w 4000–200000) was obtained from Aldrich and precipitated once from MeOH before use.

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