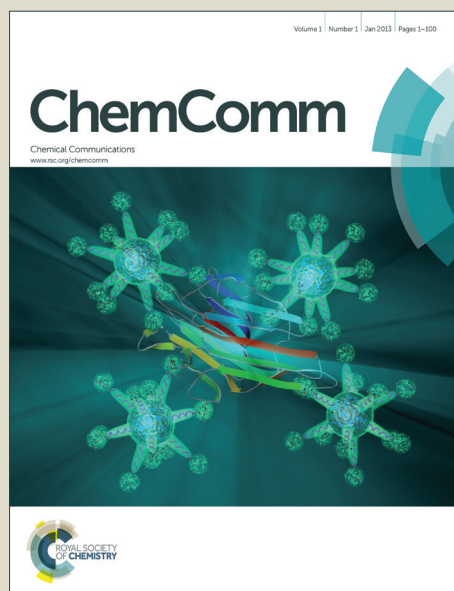


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A Catalytic Hydroesterification Process Using HCO_2Na , $\text{Ru}_3(\text{CO})_{12}$ and Alcohols for Preparing Ester Modified Polybutadienes

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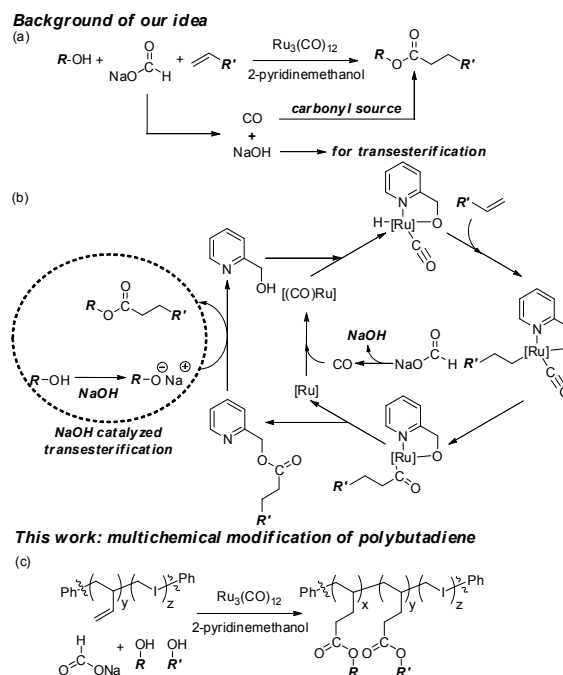
Woo-Jin Park,[§] Chang-Hee Lee,[§] Dong-Su Kim and Chul-Ho Jun,*

A method for transition metal catalyzed modification of polybutadiene was developed. Specifically, reactions of polybutadiene with alcohols and sodium formate in the presence of $\text{Ru}_3(\text{CO})_{12}$ and 2-pyridinemethanol produce ester derivatives of polybutadiene. By using this approach, selected ratios of mixed ester derivatives of polybutadiene can be produced by employing the corresponding ratio of alcohols.

Because of their broad utility, chemically modified polymers are of great interest to industrial chemists.^[1] Methods to generate these substances, especially those that utilize transition-metal catalyzed reactions of unsaturated polymers to introduce desired functional groups, have great significance.^[2] However, only a few catalytic methods for modification of unsaturated polymers have been developed thus far. Processes of this type include hydroformylation,^[3] aminomethylation,^[4] hydrocarboxylation,^[5] hydrosilylation^[6] and hydrogenation.^[7]

We developed a reaction of polybutadiene with aldehydes or primary alcohols that involves Rh-catalyzed, chelation-assisted hydroacylation.^[2a-b, d-e] In this process, which utilizes a Rh(I)/2-aminopicoline catalytic system, vinyl groups in the polybutadiene skeleton are transformed into acyl groups. Recently, many transition metal catalyzed hydroesterification methods, which transforms alkene to ester, have been developed.^[8] We also devised a new chelation-assisted hydroesterification reaction of alkenes, which employs sodium formate and alcohols along with a catalytic amount of $\text{Ru}_3(\text{CO})_{12}$ and 2-pyridinemethanol. This process converts alkenes to esters (Scheme 1a)^[9] through a pathway in which decomposition of sodium formate generates carbon monoxide to be used for carbonyl source and NaOH serves as a catalyst for the transesterification step (Scheme 1b). In this process 2-

pyridinemethanol is transformed to a pyridylmethyl ester intermediate through Ru(0) promoted carbonylation and alkene insertion, which then undergoes transesterification with the alcohol substrate to give the ester product.



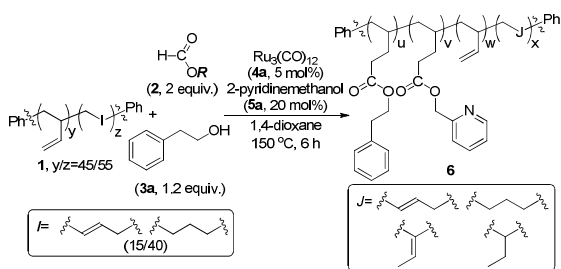
Scheme 1. (a) $\text{Ru}_3(\text{CO})_{12}$ /2-pyridinemethanol catalyzed hydroesterification of alkenes with sodium formate and alcohols (b) Proposed mechanism of hydroesterification reaction involving NaOH catalyzed transesterification step (c) Multichemical modification of polybutadiene

In our continuing studies in this area, we utilized this alkene hydroesterification process to transform polybutadiene to ester tethered analogs (Scheme 1c). In addition, we showed that the new protocol can be applied to form multiple ester modified polybutadienes where the ester ratio can be controlled by regulating the quantities of two or more alcohol starting materials. Observations made in this study are described below.

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Table 1. Optimization of the carbonyl source in the hydroesterification process^a

entry	HCOOR	ratio (%) u/v/w/x	conversion of y (%) in 1	incorporation rate of ester (%) in 6 ^e	yield (%) ^f
1		28/0/0/72	100 ^b	62	72 (6a)
2		11/9/0/80	100 ^c	24	79 (6b)
3		3/3/18/76	9 ^d	6	71 (6c)

^aAll reactions were carried out with **1** (0.416 mmol of vinyl group), **2** (0.832 mmol), **3a** (0.499 mmol), **4a** (5 mol%) and **5a** (20 mol%) in 1 mL of 1,4-dioxane.

^b38% vinyl group is reduced or isomerized. ^c56% vinyl group is reduced or isomerized. ^d47% vinyl group is reduced or isomerized. ^eIncorporation rate of ester group was calculated based on terminal phenyl in **6** and calculated as: 100 X w / (45, vinyl%). ^fIsolated yields are based on modified polybutadiene.

In order to evaluate the efficiency of the polybutadiene hydroesterification methodology and to screen various formate as carbon monoxide sources, reactions of phenyl terminated polybutadiene (**1**), containing 45% vinyl and 55% internal olefin groups, with 2-phenylethyl alcohol (**3a**) were explored. Reaction of **1** with **3a** at 150 °C for 6 h in the presence of Ru₃(CO)₁₂ (**4a**), 2-pyridinemethanol (**5a**) and sodium formate (**2a**), was found to convert 62% vinyl groups in the polymer **1** to corresponding 2-phenylethyl propanoyl ester groups in **6a** (entry 1, Table 1). Incorporation rate was determined by ¹H NMR based on the terminal phenyl group in polybutadiene **1**. The modified polymer was isolated by precipitation with methanol. When ammonium formate (**2b**) is employed as the CO source, the vinyl groups in **1** are transformed to a mixture containing 24% 2-phenylethyl and 20% 2-pyridylmethyl esters **6b** (entry 2). This result suggests that 20% of the pyridylmethyl groups do not undergo transesterification with 2-phenylethyl alcohol groups in **6a**, a likely consequence of the weaker basicity of ammonium hydroxide than that of sodium hydroxide. Calcium formate (**2c**) was also ineffective in promoting the hydroesterification process (entry 3).

Studies were carried out to explore the alcohol scope of the process (Table 2). The results show that a wide variety of simple alcohols (**3a-d**, entries 1-4, Table 2) smoothly react to produce the corresponding esterified polymers when sodium formate is utilized as the CO source. Moreover, the chelation auxiliary 2-pyridinemethanol (**5a**) participates in this reaction (entry 5) while other heteroaromatic analogues such as 2-thiophenethanol (**3e**) and 4-pyridinepropanol (**3f**) (entries 6-7) react less efficiently. The sluggishness of the latter

processes is likely a consequence of their competitive chelation to the Ru catalyst. Functionalized alcohols such as 2, 2'-(1,4-phenylene)diethanol (**3g**) and ferrocenylmethanol (**3h**) undergo smooth hydroesterification reactions with **1** to give corresponding esterified polymers **6j** and **6k** (entries 8-9). Interestingly, when 4-aminophenethyl alcohol (**3i**) is the substrate for this reaction, only ester containing polybutadiene **6i** is produced and none of the related amide is generated (entry 10). This phenomenon is a likely consequence of the fact that under the basic conditions, the alcohol moiety in **3i** is more nucleophilic than the amine group of aniline.

Table 2. Preparation of ester modified polybutadienes using sodium formate with various alcohols^a

entry	R-OH	ratio (%) v/w/x	conversion of y (%) in 1	incorporation rate of ester (%) in 6 ^e	yield (%) ^f
1		23/0/77	100	52	88 (6d)
2		21/0/79	100	46	84 (6e)
3		26/0/74	100	57	86 (6f)
4		28/0/72	100	62	72 (6a)
5		23/0/77	100	51	80 (6g)
6		16/8/76	69	37	72 (6h)
7		12/12/76	80	26	71 (6i)
8		27/0/73	100	59	70 (6j)
9		19/0/81	100	43	83 (6k)
10		11/0/89	100	24	64 (6l)
11		0/0/100	100	0	0 (6m)

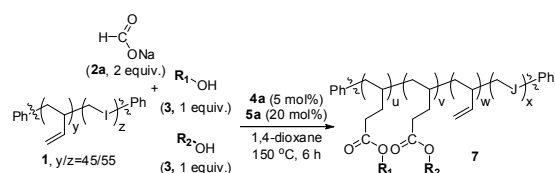
^aAll reactions were carried out with **1** (0.416 mmol of vinyl group), **2** (0.832 mmol), **3a** (0.499 mmol), **4a** (5 mol%) and **5a** (20 mol%) in 1 mL of 1,4-dioxane.

^bIncorporation rate of ester group was calculated based on the terminal phenyl in **6** and calculated as: 100 X w / (45, vinyl%). ^cIsolated yields are based on modified polybutadiene.

An investigation was conducted to determine if this protocol can be utilized to generate modified polybutadienes that contain more than one type of ester group. We observed that reaction of polybutadiene **1** with sodium formate and 1:1 ratio of 2-phenylethyl alcohol (**3a**) and heptanol (**3b**) in the presence of **4a** and **5a** at 150 °C for 6 h produces polybutadiene **7a** containing a 1:1 ratio of 2-phenylethyl and heptyl esters (Table 3, entry 1). Furthermore, the use of a 1:1 ratio of the primary alcohols **3a** and 2-thiophenylethanol (**3e**) also leads to formation of polybutadiene containing a 1:1 ratio of the corresponding esters (entry 2). The reaction of **1** with a 1:1 ratio of **3a** and the phenyl-bis-ethanol **3g** produces the modified polymer **7c** containing a 1:1 ratio of the respective esters, in which the reactivity of primary alcohol is identical regardless of mono-alcohol or di-alcohol (entry 3). However,

the ratio of the esters in the modified polybutadiene is a sensitive function of steric hindrance present in the alcohol substrates. For example, reaction of a 1:1 ratio of primary alcohol **3a** and secondary alcohol **3k**, selectively generates modified polybutadiene **6a** containing only primary alcohol derived ester groups. Moreover, exclusive formation of **6a** also takes place when a 1:1 mixture of **3a** and the tertiary alcohol **3l** are used as substrates.

Table 3. Preparation of bifunctional polybutadienes containing variable mole percentages of ester groups^a

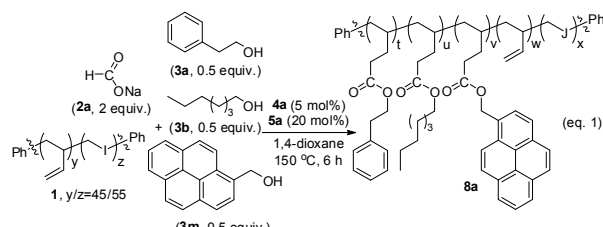


entry	alcohol		ratio (%) u/v/w/x	conversion of y (%) in 1	incorporation rate of ester in 7 (%) ^b		yield (%) ^c
	R ₁ -OH	R ₂ -OH			u:v		
1	3a	3b	11/11/0/78	100	47	50:50	83 (7a)
2	3a	3e	13/13/0/74	100	57	50:50	54 (7b)
3	3a	3g	12/12/0/76	100	52	50:50	91 (7c)
4	3a	3k	26/0/0/74	100	57	100:0	94 (6a)
5	3a	3l	25/0/0/75	100	56	100:0	88 (6a)

^aAll reactions were carried out with **1** (0.416 mmol of vinyl group), **2** (0.832 mmol), **3** (0.0416 mmol), **4a** (5 mol%) and **5a** (20 mol%) in 1 mL of 1,4-dioxane.

^bIncorporation rate was determined by ¹H NMR. ^cIsolated yields are based on modified polybutadiene.

As expected, modification reaction of polybutadiene **1** with a 1:1:1 ratio of the three primary alcohols **3a**, **3b** and **3m** forms a 1:1:1 ratio of the corresponding ester incorporated polybutadiene **8a** (eq. 1).

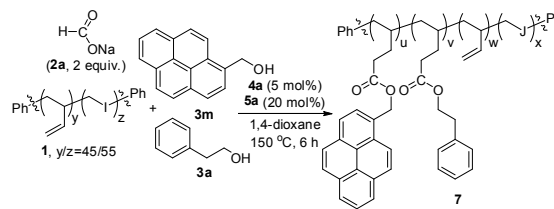


ratio (%) t/u/v/w/x	conversion of y (%) in 1	incorporation rate of esters in 8a (%)		yield (%)
		t:u:v		
9/9/9/0/73	100	57	33:33:33	95 (8a)

In the final phase of this effort, we demonstrated that the new modification strategy can be utilized to prepare polybutadienes containing a fluorescent label. For this purpose, reaction of polybutadiene **1** and sodium formate with a 5:95 ratio of pyrenylmethyl alcohol (**3m**) and 2-phenylethyl alcohol (**3a**) was carried out under the standard conditions. This process was observed to generate polybutadiene derivative **7d** containing a 5:95 ratio of pyrenylmethyl and 2-phenylethyl esters (entry 1 of Table 4). As the ratio of **3m** and

3a employed as alcohol substrates in the reaction is increased from 10:90 to 50:50, the proportion of pyrenylmethyl ester groups in modified polymer increases in a proportional manner (entries 2-5). The results again show that the relative percentages of the ester groups in the polymer can be controlled precisely by simply adjusting the ratio of starting alcohols.

Table 4. Preparation of bifunctional polybutadiene with variable mole percentages of pyrenylmethyl ester groups^a



entry	alcohol (2 equiv.) ratio of 3m:3a		ratio (%) u/v/w/x	conversion of y (%) in 1	incorporation rate of esters in 7 (%) ^b		yield (%) ^c
	w:x						
1	5:95	1/20/0/79	100	46	5:95	75 (7d)	
2	10:90	2/21/0/77	100	50	10:90	78 (7e)	
3	20:80	5/19/0/76	100	54	20:80	77 (7f)	
4	30:70	7/16/0/77	100	52	30:70	79 (7g)	
5	50:50	11/11/0/78	100	47	50:50	84 (7h)	
6	100:0	23/0/0/77	100	52	100:0	89 (7i)	

^aAll reactions were carried out with **1** (0.416 mmol of vinyl group), **2** (0.832 mmol), **3m**, **3a**, **4a** (5 mol%) and **5a** (20 mol%) in 1 mL of 1,4-dioxane at 150 °C.

^bIncorporation rate was determined by ¹H NMR. ^cIsolated yields are based on modified polybutadiene.

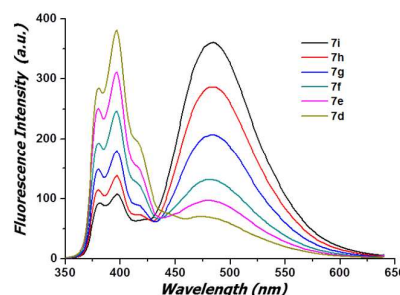


Fig 1. Excimeric and monomeric fluorescence of **7d-i** in MeCN/DCM(1/1)

The spectra displayed in Figure 1 demonstrate that polybutadiene **7d**, containing 5% pyrenylmethyl ester groups, has a fluorescent emission maximum at 380 nm, which corresponds to emission from a monomeric excited state. However, the intensities of the monomeric emission band at 380 nm in fluorescence spectra of modified polybutadienes decrease as the proportion of the pyrenylmethyl ester group increases (**7e**, **7f**, **7g**, and **7h**). In addition, simultaneously a maxima appears in the spectra at 484 nm associated with excimer emission arising by intramolecular π - π interactions between the pyrene groups.^[10] The intensity of the excimer emission band is highest when the modified polybutadiene contains only (**7i**) pyrenylmethyl ester groups.

The selective metal cation sensing ability of polybutadiene **7i**, containing only pyrenylmethyl ester groups, was explored. For

this purpose, fluorescence titrations of **7i** with various metal ions were performed (Figure 2).

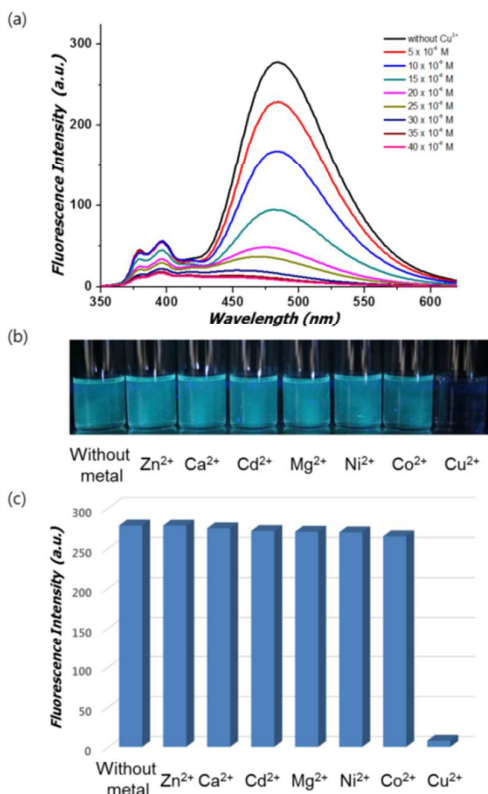


Fig 2. (a) Fluorescence titration spectra of **7i** with different concentration of CuClO_4 (b) Images of solutions of **7i** containing $40 \times 10^{-6} \text{ M}$ of various metal(II) cations upon irradiation at 365 nm (c) Fluorescence intensities at 484 nm of **7i** with various metal(II) cation ($40 \times 10^{-6} \text{ M}$) excited at 330 nm

As can be seen by viewing the emission spectra displayed in Figure 2a, addition of Cu^{2+} to a MeCN/DCM(1/1) solution of **7i** promotes a decrease in the intensity of the excimer fluorescence band, which completely disappears when the concentration of Cu^{2+} reaches $40 \times 10^{-6} \text{ M}$ (Figure 2a). The results of fluorescence experiments with Zn^{2+} , Ca^{2+} , Cd^{2+} , Mg^{2+} , Ni^{2+} and Co^{2+} ($40 \times 10^{-6} \text{ M}$) (Figure 2b-c) demonstrate that none of these metal ions quench the excimer emission from **7i**. These observations show that pyrenylmethyl ester containing polybutadiene **7i** serves as a highly selective sensor of Cu^{2+} .

In the investigation described above, we developed a new chelation assisted hydroesterification methodology for the preparation of modified polybutadienes. Specifically, reaction of polybutadiene with sodium formate and an alcohol in the presence of $\text{Ru}_3(\text{CO})_{12}$ and 2-pyridinemethanol efficiently produces a modified polymer containing ester groups. We have shown that this protocol can be employed to prepare polybutadienes containing two or more different ester groups in ratios that can be controlled by regulating the relative amounts of the alcohol substrates. Finally, a polybutadiene modified with pyrenylmethyl ester groups was synthesized and demonstrated to serve as a selective Cu^{2+} sensor. Further

applications of the new methodology are being developed in our continuing studies in this area.

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