Catalytic Hydrocarboxylation and Hydroesterification Reactions of 1,2-Polybutadiene

Abdelaziz Nait Ajjou and Howard Alper*

*Department of Chemistry, University of Ottawa, 10 Marie Curie,
Ottawa, Ontario, Canada K1N 6N5*

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ABSTRACT: Using different homogeneous catalytic systems, the hydrocarboxylation of 1,2-polybutadiene (M_w 2400) was achieved with partial to full conversion of pendant double bonds in a highly regioselective manner. The use of $Pd(OAc)_2$/1,4-bis(diphenylphosphino)butane (dppb)/HCOOH or Pd(II)/dppb/ROH leads, respectively, to linear polyacids or polyesters. The extent of hydroesterification is controlled by the reaction time, temperature, and nature of the catalyst.

Introduction

Functional polymers are generally prepared by the polymerization of monomers containing the desired functional groups. As these polymerizations are sometimes associated with potential problems, much attention has been paid to the development of the catalytic functionalization of diene-based elastomers.[1−19] The production of polymers with carboxylated backbones is of particular interest due to potential applications of such polymers in films and surface coating.[20] Catalytic processes involving the use of carbon monoxide are an important strategic approach to such compounds.

One of the most effective processes for olefin functionalization is the hydrocarboxylation[21] and related hydroesterification[22] reactions. By judicious choice of the catalyst and added ligand, these transformations lead to carbonylated compounds in excellent yields with high regiochemical control.

We report herein the palladium-catalyzed hydrocarboxylation and hydroesterification of 1,2-polybutadiene, leading to linear polyacids and polyesters, respectively. The polymer products were characterized by infrared and nuclear magnetic resonance (^1H, ^{13}C) spectroscopy and by gel permeation chromatography.

Experimental Section

Materials. 1,2-Polybutadiene (M_w 2400), containing more than 90% vinyl pendant groups, was provided by Nisso Iwai Canada Ltd. (made in Japan by Nippon Soda Co.).

$Pd(OAc)_2$, 1,4-bis(diphenylphosphino)butane (dppb), formic acid, and 1,2-dimethoxyethane (DME) were purchased from Aldrich Chemical Co., *p*-toluenesulfonic acid was obtained from Fisher Scientific Co., and $PdCl_2$ and $Pd(PPh_3)_4$ were purchased from Strem Chemicals. Pd-clay was synthesized by anchoring 2,2′-bipyridine in the interlayers of montmorillonite and subsequent complexation with $Pd(OAc)_2$ (Pd content 2.93 wt %, and $d_{(001)}$ expansion of Pd-clay was determined to be 6.7 Å).[23] $PdCl_2(PPh_3)_2$[24] and $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$[25] were prepared according to literature methods. Solvents were dried and distilled prior to use.

Instruments. IR spectra were recorded using a Bomem MB100-C15 (FT-IR) instrument. ^1H and ^{13}C NMR spectral determinations were made on either a Varian Gemini 200 or Bruker 500 MHz spectrometer. The molecular weight averages of polyacids were measured by gel permeation chromatography (GPC) using a Waters M-6000 instrument with a Waters 410 differential refractive index detector at 35 °C, tetrahydrofuran (THF) as the solvent, and polybutadiene standards for calibration. In the case of polyesters, the molecular weight averages were determined using a Perkin-Elmer 250 GPC with a UV detector set at 254 nm, with chloroform as the solvent at room temperature, and polystyrene standards for calibration. pHmetric titrations of polyacids were performed using a Corning155 pH/ion meter.

Hydrocarboxylation Procedures. (1) Using $Pd(OAc)_2$/dppb/HCOOH. In a 45 mL autoclave equipped with a glass liner containing a stirring bar and 4 mL of DME was placed palladium acetate (4.5 mg, 0.02 mmol) and dppb (17 mg, 0.04 mmol). To this mixture was added a solution of 1,2-polybutadiene (270 mg in 1 mL of DME; equivalent to 5 mmol of vinyl groups) and then formic acid (460 mg, 10 mmol). The autoclave was purged with carbon monoxide, pressurized to 100 psi, and heated at 150 °C for 21 h. The autoclave was then cooled to room temperature, CO was vented, and the reaction mixture was filtered and evaporated to near dryness. Ether (30 mL) was added, and the polymer product precipitated instantly. The latter was solubilized using 2 M NaOH (30 mL). The layers were separated, and the ether layer was dried ($MgSO_4$) and evaporated. The ^1H NMR spectrum of the solid residue did not show any traces of the starting polymer. The aqueous layer was acidified with 30 mL of HCl (6 M), and the precipitated polyacid product was collected by filtration. Some acetone was also used to collect small amounts of polyacid adhering to the glass wall. The polyacid was dried in vacuo.

(2) Using Pd-clay/dppb/HCOOH. The above procedure was followed, except that Pd-clay (42 mg, 0.0116 mmol) was used instead of palladium acetate, and the reaction time was increased to 27 h.

(3) Using $PdCl_2/CuCl_2/O_2$. Carbon monoxide was bubbled through a solution of THF (40 mL) and water (1.0 mL) for 15 min. Palladium chloride (140 mg, 0.78 mmol) and 12 M HCl (1.0 mL) were added, and when the $PdCl_2$ was completely dissolved, $CuCl_2{\cdot}2H_2O$ (260 mg, 1.55 mmol) was added to the mixture. Oxygen was bubbled through the solution at a rate similar to that of CO (controled by flowmeter). A solution of 1,2-polybutadiene (200 mg in 5 mL of THF; equivalent to 3.7 mmol of vinyl groups) was added, and the mixture was stirred at room temperature, under carbon monoxide and oxygen for 40 h. The workup of the product was effected using the above procedure. The polyacids are soluble in acetone and methanol.

Titration of Carboxylic Acid Groups. An exact weighted amount of the sample (50−200 mg) was dissolved in 20 mL of 0.2 N sodium hydroxide solution. The resulting solution, and the blank prepared containing only 20 mL of 0.2 N sodium hydroxide solution, were titrated with 0.25 N hydrochloric acid using a Corning 155 pH/ion meter.

Titration of Vinyl Groups (Determination of Iodine Value).[26] The polyacid sample (100 mg) was dissolved in a mixture of chloroform and THF (1/1, 20 mL) in a 250 mL round-bottom flask. After complete dissolution, 10 mL of a 0.2 N iodine monochloride solution in chloroform was added. The solution was stirred in the dark for 5 h. Freshly prepared 10% potassium iodide solution (50 mL) was added, and the

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mixture was titrated with 0.1 N sodium thiosulfate solution. When the aqueous layer was decolorized, 2−3 mL of starch solution was added, and the mixture was vigorously stirred until both layers were decolorized. A blank prepared containing 10 mL of 0.2 N iodine monochloride, 10 mL of THF, and 10 mL of $CHCl_3$ was evaluated in the same manner.

The iodine value (IV, measure of the number of double bonds), defined as the amount of iodine bonded by 100 g of sample, is calculated according to eq 1, where V_1 is the number

$$\mathrm{IV} = 1.269(V_2 - V_1)/m \qquad (1)$$

of milliliters of 0.1 N sodium thiosulfate solution for the sample, V_2 is the number of milliliters of 0.1 N sodium thiosulfate solution for the blank, and m is the sample weight in grams.

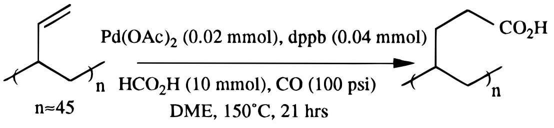
Hydroesterification Procedure. In a 45 mL autoclave equipped with a glass liner containing a stirring bar and DME (4 mL) was added the palladium complex (0.04 mmol), dppb (34 mg, 0.08 mmol), and *p*-toluenesulfonic acid (*p*-TsOH) (0−16 mg, 0−0.08 mmol) . To this mixture was added a solution of 1,2-polybutadiene (270 mg in 1 mL of DME; equivalent to 5 mmol of vinyl groups) followed by 2 mL of alcohol. The autoclave was purged with carbon monoxide, pressurized to 600 psi, and then heated at the desired temperature for 16−72 h. The autoclave was cooled to room temperature, CO was vented, the reaction mixture was filtered, and the filtrate was concentrated by rotary evaporation. The polyester product was extracted with ethyl acetate, and the organic layer was dried ($MgSO_4$) and evaporated. A mixture of ether (10 mL) and acetone (10 mL) was added, and the undissolved salts and dppb precipitated. After filtration, the filtrate was concentrated. The latter procedure was repeated, several times, until no precipitate was observed. The resulting polyester was dried in vacuo. The polyesters are soluble in common organic solvents.

Results and Discussion

(1) Catalytic Hydrocarboxylation of 1,2-Polybutadiene.

Recent publications have described the hydrocarboxylation of polybutadienes catalyzed by $PdCl_2(PPh_3)_2$ in the presence of $SnCl_2$ or PPh_3, at 90 and 170 °C, respectively.[16−18] Although high conversions of the pendant double bonds to terminal carboxylic acids were obtained with $SnCl_2$, high CO pressures were required for these reactions. At approximately the same time, a new process for the hydrocarboxylation of monoolefins based on formic acid was developed, resulting in the formation of straight-chain acids as the major products.[21a−c] This method can tolerate the presence of a variety of functional groups and operates under low pressures of carbon monoxide. We now describe the use of this and related methods for the hydrocarboxylation of 1,2-polybutadiene.

Treatment of 1,2-polybutadiene with formic acid (2 equiv relative to the number of vinyl groups) and CO (100 psi), catalytic amounts of palladium acetate, and dppb in DME for 21 h at 150 °C (eq 2) afforded the hydrocarboxylated polymer (Table 1, entry 1).



(2)

The IR spectrum (neat) of the product shows the appearance of a broad stretching absorption for the hydroxy groups at 3650−2500 cm^{-1} and an intense carbonyl stretching band at 1708 cm^{-1}. The characteristic absorptions due to the unsaturated units at 3073, 1640, and 910 cm^{-1} completely disappeared. The ^{13}C NMR spectrum of the product exhibits only *one* carbonyl signal at 175 ppm. Based on spectroscopic data obtained in the previous studies of hydrocarboxylated polybutadienes,[16−18] the resonance was assigned to the carboxylic acid groups at the terminal carbon atom of the pendant double bonds. This NMR result, together with the ^1H NMR spectrum and iodine value determinations, shows complete saturation of vinyl groups. The molecular weight of this linear polyacid, determined by GPC as 4900 (Table 2, entry 1), is close to the calculated molecular weight (4500). These results are further supported by pHmetric titration (Figure 1) and the molecular weight distribution (M_w/M_n = 2.96), indicating high selectivity to hydrocarboxylation and no cross-linking or chain scission.

Table 1. Titrations of Polycarboxylic Acids Obtained Using Different Pd-Based Systems

entry	catalytic system	IV	$CH{=}CH_2$ (mmol/g)	CO_2H (mmol/g)	poly-acid
1[a]	$Pd(OAc)_2/HCO_2H$/dppb	0	0	10	**1**
2[b]	$Pd(OAc)_2/HCO_2H$/dppb	205	8.1	5.5	**2**
3[c]	$Pd(OAc)_2/HCO_2H$/dppb	190	7.5	5.25	**3**
4[d]	Pd-clay/HCO_2H/dppb	228	9	5	**4**
5[e]	$PdCl_2/CuCl_2/O_2$/CO	216	8.5	3.82	**5**

[a] Conditions: $Pd(OAc)_2$ (0.02 mmol), dppb (0.04 mmol), HCO_2H (10 mmol), CO (100 psi), DME, 150 °C, 21 h. [b] Conditions: $Pd(OAc)_2$ (0.02 mmol), dppb (0.04 mmol), HCO_2H (5 mmol), CO (100 psi), DME, 150 °C, 21 h. [c] Conditions: $Pd(OAc)_2$ (0.02 mmol), dppb (0.04 mmol), HCO_2H (5 mmol), CO (100 psi), DME, 150 °C, 40 h. [d] Conditions: Pd-clay (42 mg, 0.0116 mmol), dppb (0.04 mmol), HCO_2H (10 mmol), CO (100 psi), DME, 150 °C, 27 h. [e] Conditions: $PdCl_2$ (0.78 mmol), $CuCl_2$ (1.55 mmol), O_2 and CO (1 atm), THF, room temperature, 40 h.

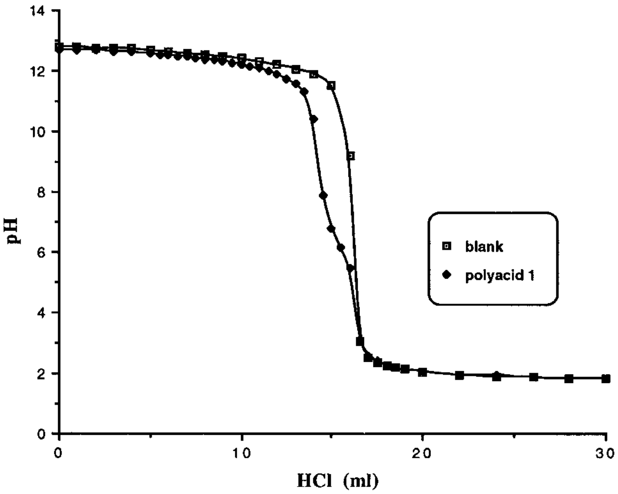


Figure 1. pHmetric titration (using 0.25 M HCl) of a solution containing polyacid **1** (50 mg) and NaOH (20 mL, 0.2 M).

When the previous experimental conditions were used, except for the reduction of the number of millimoles of formic acid from 10 to 5, partial conversion occurs as shown by NMR, pHmetric titration, and iodine value measurements, the latter indicating that only 41% of the pendant vinyl groups react, with excellent selectivity for hydrocarboxylation (97%) (Table 2, entry 2). The extension of the reaction time to 40 h (Table 1, entry 3) led to a slight increase of the percent conversion acompanied by extensive cross-linking. The molecular weight (87 000) is significantly higher than that calculated, and there is broadening of the molecular weight distribution (Table 2, entry 3). The presence of only one carbonyl signal at 175 ppm in the ^{13}C NMR spectrum indicates that cross-linking occurred, likely via vinyl groups.

Table 2. Conversions and Selectivities of Hydrocarboxylation Processes and Products Molecular Weight Averages

polyacid	convrsn[a] (%)	selectvy[b] (%)	M_w	M_n	M_w/M_n
1	100	100	4900	1700	2.96
2	41	97	3396	2208	1.54
3	47	80	87000	2400	36.5
4	37	95	9200	2100	4.40
5	44	56	59000	2600	22.8

[a] Conversions are calculated according to eq 5. [b] Selectivities are calculated according to eq 6.

Prior work in our laboratory has shown that the anchoring of palladium to a clay can generate an effective catalytic system for the reductive carbonylation of nitro compounds to urethanes,[27] the oxidative carbonylation of amines,[28] and the hydroesterification of olefins.[22d] When montmorillonitebipyridinepalladium acetate (Pd-clay) was used as catalyst instead of palladium acetate (Table 1, entry 4), only 37% of the vinyl groups react but with high selectivity for hydrocarboxylation (95%). The molecular weight of this unsaturated polyacid was 9200.

Hydrocarboxylation did occur under oxidative carbonylation conditions[29] using palladium chloride and cupric chloride as catalysts, and carbon monoxide and oxygen in aqueous acidic tetrahydrofuran, at room temperature and 1 atm of pressure (Table 1, entry 5). The iodine value and pHmetric titrations reveal that 44% of the vinyl groups reacted with only 56% selectivity for hydrocarboxylation (Table 2, entry 5). The ^{13}C NMR of this cross-linked polyacid ($M_w = 59\,000$) indicates the presence of two types of carbonyl groups, that of an acid attached to the backbone (177 ppm) and the other of a linear acid in a pendant side chain (175 ppm).

The previous data for conversions and selectivities were obtained, using the following calculations, which assume that the molecular weight of the olefin unit (54 g/mol) does not change during cross-linking and hydrogenation processes:

$$m = 100n_{\mathrm{COOH}} + 54(n' + n_{\mathrm{c=c,left}}) \qquad (3)$$

$$\sum n_i = n_{\mathrm{COOH}} + n' + n_{\mathrm{c=c,left}} \qquad (4)$$

$$\text{conversion} \qquad C = 1 - (n_{\mathrm{c=c,left}}/\sum n_i) \qquad (5)$$

$$\text{selectivity} \qquad S = n_{\mathrm{COOH}}/C\sum n_i \qquad (6)$$

where m is the weight of the product sample (in mg) used for titrations. n', $n_{\mathrm{c=c,left}}$, and n_{COOH} are respectively the numbers (in mmol) of vinyl groups that are cross-linked and hydrogenated, unreacted, and transformed to acid groups.

(**2**) **Catalytic Hydroesterification of 1,2-Polybutadiene.** The hydroesterification of polybutadienes catalyzed by cobalt[15] and palladium[14] compounds has been the subject of several recent patents. These processes are not selective, since in addition to the desired carboxylic ester products, cyclic ketones were obtained in the former case while other oxo groups were detected using palladium.

The principal goal of the following work was to obtain complete conversion of 1,2-polybutadiene to polyesters and to determine the influence of the temperature, reaction time, and nature of the catalyst on the degree of hydroesterification.

Table 3. Hydroesterification of 1,2-Polybutadiene Using $Pd(OAc)_2$ (0.04 mmol), dppb (0.08 mmol), *p*-TsOH (0.08 mmol), EtOH (2 mL), CO (600 psi), and DME

entry	temp (°C)	time (h)	convrsn[a] (%)	polyester
1[b]	100	16	0	
2	100	16	39	**6**
3	100	72	53	**7**
4	150	72	91	**8**
5[c]	170	72	100	**9**

[a] Conversions are calculated according to eq 7. [b] Without *p*-TsOH. [c] With 96% selectivity estimated from ^{1}H NMR, using diphenylfulvene as internal standard.

The extent of hydroesterification (conversion of vinyl to ester groups; C) was estimated from the integration of ^{1}H NMR spectra using the following relationships:

$$C = I_{\mathrm{OCH_2}}/(I_{\mathrm{OCH_2}} + I_{\mathrm{c=c}}) \quad \text{(in the case of ethanol)} \qquad (7)$$

$$C = 2I_{\mathrm{OCH_3}}/(2I_{\mathrm{OCH_3}} + 3I_{\mathrm{c=c}} \quad \text{(in the case of methanol)} \qquad (8)$$

where $I_{\mathrm{c=c}}$ is the integration of unreacted double-bond proton signals at 4.9 ppm, $I_{\mathrm{OCH_2}}$ is the integration of the OCH_2 proton signals at 4.0 ppm (in the case of ethanol), and $I_{\mathrm{OCH_3}}$ is the integration of the methoxy proton signals at 3.6 ppm (in the case of methanol).

No reaction occurred when 1,2-polybutadiene was treated with carbon monoxide (600 psi) and ethanol in DME at 100 °C for 16 h in the presence of dppb and $Pd(OAc)_2$ as catalyst. When the reaction was repeated with added *p*-TsOH, hydroesterification occurred, with 39% conversion of the reactant pendant vinyl groups (Table 3, entries 1 and 2). The influence of *p*-TsOH was previously examined in the hydroesterification of styrene catalyzed by $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$.[22c]

In the IR spectrum of the product, the characteristic absorption bands attributed to the pendant vinyl groups at 3073, 1640, and 910 cm^{-1} decrease while the ethoxycarbonyl group bands appear at 1734 and 1181 cm^{-1}. The signals for the methylene and methyl protons of the ethoxy group appear in the ^{1}H NMR at 4.0 and 1.2 ppm, respectively. In the ^{13}C NMR spectrum, the resonances at 14.1 and 60.1 ppm are assigned to the methyl and methylene carbons, with a carbonyl signal at 173.8 ppm. The conversion of the vinyl units to ethoxycarbonyl groups increased with increasing reaction time and temperature (Table 3, entries 3–5). Figure 2 shows that the conversions obtained by ^{1}H NMR agreed with the values determined by the iodine value method. The other polyesters obtained exhibit almost identical characteristics in IR and NMR spectra with varying degrees of intensity. Full conversion of 1,2-polybutadiene to the ethyl polyester was achieved at 170 °C. The regioselectivity of this reaction was determined by saponification of the formed polyesters in a mixture of THF and dilute NaOH, followed by hydrolysis of the corresponding sodium salts to polyacids. The polyacids showed only one carbonyl resonance at 175 ppm in the ^{13}C NMR spectrum, indicating that the ethoxycarbonyl group is attached to the terminal carbon atom of the pendant double bonds.[16–18] Therefore, the polyesters obtained using the previous conditions are linear (eq 9).

The results in Table 4 indicate that the molecular weight averages increase with increasing degree of hydroesterification of the parent 1,2-polybutadiene. The calculated and experimental M_w for the fully hydro-

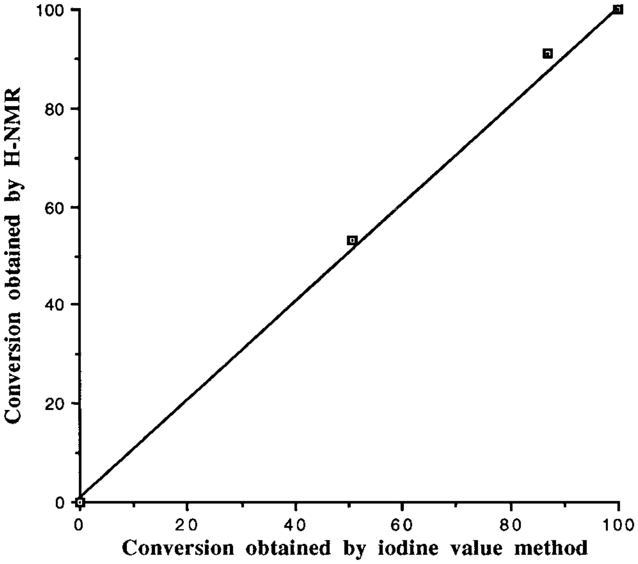
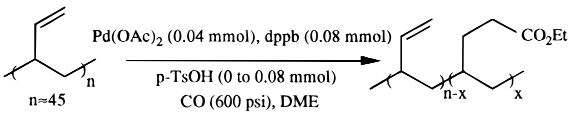


Figure 2. Conversions obtained by ^{1}H NMR vs the conversions obtained by the iodine value method.

Table 4. Comparison of 1,2-Polybutadiene and Ethyl Polycarboxylic Ester Molecular Weight Averages

entry	polymer	calcd M_w	exp M_w	exp M_n	M_w/M_n
1	1,2-polybutadiene		2400	1500	1.59
2	**7**	4165	4069	2641	1.54
3	**8**	5430	5562	2051	2.71
4	**9**	5730	5693	2643	2.15



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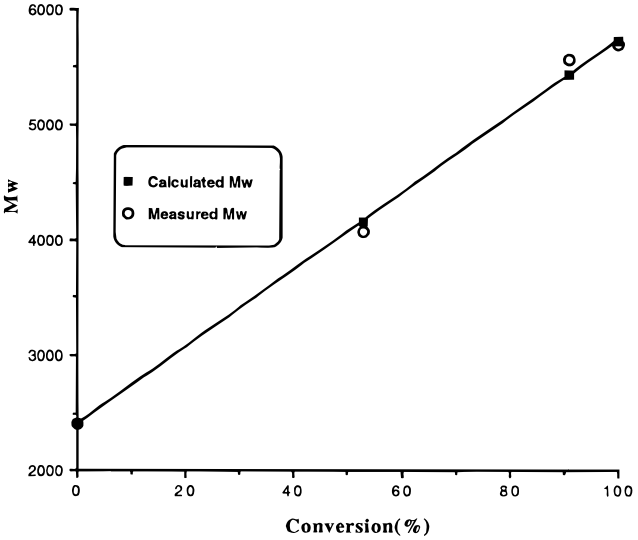

Figure 3. Molecular weight vs the percent conversion to ethyl polyester by the hydroesterification of 1,2-polybutadiene (Table 4).

Table 5. Hydroesterification of 1,2-Polybutadiene Using $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ (0.04 mmol), dppb (0.08 mmol), *p*-TsOH (0.08 mmol), EtOH (2 mL), CO (600 psi), and DME

entry	temp (°C)	time (h)	convrsn[a] (%)	polyester
1[b]	100	16	0	
2	100	16	17	**10**
3	100	72	21	**11**
4	150	72	42	**12**
5	170	72	64	**13**

[a] Conversions are calculated according to eq 7. [b] Without *p*-TsOH.

Table 6. Hydroesterification of 1,2-Polybutadiene Using Different Palladium Catalysts (0.04 mmol), dppb (0.08 mmol), *p*-TsOH (0.08 mmol), MeOH (2 ml), CO (600 psi), and DME, 170 °C, 72 h

entry	catalyst	convrsn[a] (%)
1[b,c]	$Pd(OAc)_2$	100
2	$PdCl_2(PPh_3)_2$	100
3	$((\pi\text{-allyl})PdCl)_2$	78
4[d]	$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$	52
5	$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$	80
6	$Pd(PPh_3)_4$	0

[a] Conversions are calculated according to eq 8. [b] Measured M_w = 5010, M_n = 3937, and M_w/M_n = 1.27. Calculated M_w = 5130. [c] With 96% selectivity estimated from ^{1}H NMR, using diphenylfulvene as internal standard. [d] Reaction temperature 150 °C.

esterified 1,2-polybutadiene are in excellent accord (Table 4, entry 4). An increase in the polymer molecular weight averages is expected since the hydroesterification with ethanol of one vinyl group will increase the molecular weight of the olefin unit from 54 to 128 g/mol. Thus, according to the eq 9, the calculated M_w can be expressed by the following relationship:

$$M_w = M°_w + 74nC = 2400 + 3330C \qquad (10)$$

where $M°_w$ is the average molecular weight of 1,2-polybutadiene and C represents the percent conversion of the vinyl groups. Remarkably, Figure 3 shows that M_w increases linearly in proportion to the conversion of vinyl groups and that there is no noticeable deviation from $M_w = f(C(\%))$, suggesting that high selectivities toward hydroesterification were obtained, and no side reaction occurred under our conditions. The polydispersity indexes (1.54−2.71) of these polyesters are excellent.

When $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ was used as the catalyst instead of $Pd(OAc)_2$ for the hydroesterification reaction, the same trends were observed concerning the influence of *p*-TsOH, reaction time, and temperature. However, the cationic palladium complex is less reactive than $Pd(OAc)_2$ (Table 5).

Different palladium complexes were used for the hydroesterification of 1,2-polybutadiene, using methanol instead of ethanol at 170 °C (Table 6). $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$ afford full conversion of vinyl pendant groups whereas $((\pi\text{-allyl})PdCl)_2$ and $[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ give only ~80% conversion. The palladium(0) complex, $Pd(PPh_3)_4$, is, however, completely inactive. The molecular weight of methyl polyester obtained in the case of $Pd(OAc)_2$ was determined to be 5010, close to the calculated molecular weight value of 5130.

The infrared spectrum of the product exhibits methoxycarbonyl stretching bands at 1736 (C=O) and 1188 cm^{-1} (C−O). The protons for the methoxy group appear at 3.6 ppm in the ^{1}H NMR spectrum, and the methyl and carbonyl carbons occur at 51.4 and 174.1 ppm, respectively, in the ^{13}C NMR spectrum. The transformation of polyesters to the corresponding polyacids indicates the regioselectivity of the hydroesterification to straight chain polyesters.

Conclusions

Straight-chain saturated polycarboxylic acids were easily synthesized by the hydrocarboxylation of 1,2-polybutadiene using formic acid and catalytic amounts of Pd(OAc)$_2$ and dppb, under a low pressure of carbon monoxide (100 psi). This is an excellent method for the synthesis of the polyacid.

The use of the Pd(II)/dppb/*p*-TsOH system led to polyesters with various degrees of unsaturation. Fully saturated polyesters (e.g. polymer **9**) can be obtained in this manner using a higher carbon monoxide pressure (600 psi) than for the hydrocarboxylation reaction. In contrast to prior art, no cyclic ketones or other oxo-containing products were observed in these reactions.

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