Catalytic Oxidation of Polybutadienes Based on a Wacker-Type Reaction

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ABSTRACT: Full conversion of polybutadienes to polyketones was easily achieved using low oxygen pressure and catalytic amounts of palladium chloride and copper chloride in 1,2-dimethoxyethane at 80 °C. The conversions and selectivities of this Wacker-type reaction are controlled by the reaction conditions. The polyketone products were characterized by ^{1}H and ^{13}C NMR and infrared spectroscopy and by gel permeation chromatography.

Introduction

Polyketones are very important materials due to the presence of carbonyl groups. In addition to their photodegradable nature,[1] they are easily converted to other functionalized polymers[2] including electroconductive polymers.[3]

Polyketones are usually synthesized by the copolymerization of α-olefins and carbon monoxide[4] or by polymerization of unsaturated ketones.[5] Among the major problems encountered, however, in such polymerization processes are the occurrence of side reactions like cross-linking or the difficulty of controlling the polymerization reaction.[6]

We report herein the catalytic oxidation of polybutadienes, using a simple Wacker-type method consisting of oxygen and catalytic amounts of palladium chloride and copper chloride. The polyketone products were characterized by infrared and nuclear magnetic resonance (^{1}H, ^{13}C) spectroscopy and by gel permeation chromatography. The conversions were estimated using ^{1}H NMR spectroscopy.

Experimental Section

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

Phenyl-terminated polybutadiene **2**, containing 25% pendant double bonds and 40% trans backbone, was purchased from Aldrich Chemical Co., as was polybutadiene **3**, having 20% pendant double bonds and 80% cis and trans backbone (molecular weights and polydispersities for **1**−**3** are given in Table 1). $PdCl_2$ was obtained from Fisher Scientific Co. $CuCl_2{\cdot}2H_2O$ was purchased from BDH Ltd. Oxygen was obtained from Air Products Co. 1,2-Dimethoxyethane (DME) was dried and distilled prior to use.

Instruments. IR spectra were recorded using a Bomem MB100-C15 (FT-IR) instrument. ^{1}H and ^{13}C NMR spectral determinations were made on either a Varian Gemini 200 or Bruker 500 MHz spectrometer using DMSO-d_6 or $CDCl_3$ as the solvent. Solid state ^{13}C NMR spectra measurements were made on a 200 MHz Bruker spectrometer. Molecular weights and molecular weight distributions were measured at 45 °C by gel permeation chromatography (Waters high-pressure instrument Model 510 pump), using a series of 10 μm particle size μ.Styragel columns HT 3, HT 4, and HT 5 with effective molecular weight ranges of 500−30 000, 5000−600 000, and 50 000−4 × 10^6, respectively, and a differential refractometer (Model 410). Tetrahydrofuran was used as eluant at a flow rate of 1 mL/min, and a sample concentration of 1 mg/mL was used. Polybutadiene narrow standards were used for calibration.

Table 1. Molecular Weights and Polydispersities of Starting Polybutadienes

polymer no.	M_w	M_n	M_w/M_n
1	2633	2137	1.23
2	3137	2012	1.56
3	5169	4983	1.04

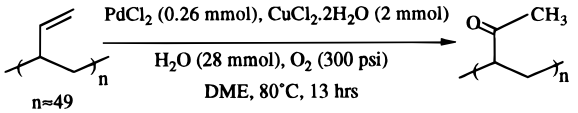
Catalytic Oxidation Procedure. In a 45 mL autoclave equipped with a glass liner containing a stirring bar and 6 mL of DME was placed palladium chloride (46 mg, 0.26 mmol) and copper chloride dihydrate (44−340 mg, 0.26−2 mmol). To this mixture was added a solution of polybutadiene (270 mg in 4 mL of DME; equivalent to 5 mmol of double bonds) and then 0.5 mL of water (28 mmol). The autoclave was purged with oxygen, pressurized to 100−300 psi, and heated at 80−120 °C for the required reaction time. The autoclave was then cooled to room temperature, O_2 was vented, and the reaction mixture was filtered. The polyketone product was extracted with ethyl acetate and the organic layer was dried ($MgSO_4$) and evaporated. The resulting polyketone was dried in vacuo.

Caution. At the end of the reaction and before removing the solvent the presence of residual peroxides was checked by known methods.[7] The analysis showed no detectable quantities of peroxides.

Results and Discussion

To our knowledge, only one method has been reported on the catalytic oxidation of polybutadienes to polyketones.[8] This process involves the oxidation of these polymers to the corresponding polyketones using *tert*-butyl hydroperoxide in the presence of $[Pt(Ph_2PCH{=}CHPPh_2)CF_3(CH_2Cl_2)]^+$ and resulted in only 57% overall conversion. We now report our results concerning the oxidation of polybutadienes using molecular oxygen in a Wacker-type reaction.

No reaction occurred when 1,2-polybutadiene **1** was allowed to react at 80 °C with oxygen (300 psi) in the presence of palladium chloride and copper chloride in benzene under phase transfer catalysis conditions[9] (Table 2, entry 1). However, the use of DME as solvent leads to full conversion of vinyl groups to acetyl groups (Table 2, entry 2). The same result was obtained (eq 1)



(1)

when the reaction was run in the absence of the phase

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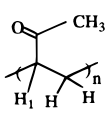
Table 2. Oxidation of 1,2-Polybutadiene 1 Using $PdCl_2$ (0.26 mmol), $CuCl_2 \cdot 2H_2O$ (2 mmol), H_2O (0.5 mL), O_2 (300 psi), and DME, 80 °C

entry	reaction time (h)	conversion (%)
1[a,b]	13	0
2[a]	19	100
3	13	100
4[c]	19	100[d]
5	44	100[e]
6[f]	16	0
7[g]	43	partial[h]

[a] Cetyltrimethylammonium bromide (0.6 mmol) was used as the phase transfer catalyst. [b] Benzene was used as the solvent. [c] The reaction temperature was 120 °C. [d] The starting polymer was completely converted to carbonylated products (CO signal at 170−177 ppm). [e] The polymer product contains acetyl groups (~210.1−211.1 ppm) and other carbonyl groups (170−177 ppm). [f] The reaction was run at room temperature. [g] Oxygen at 100 psi was used. [h] Cross-linked unsaturated polyketone was obtained.

Chart 1



	Chemical shifts (ppm)			
	^{13}C NMR		^{1}H NMR	
	Our data	Ref. 10	Our data	Ref. 11
CH_3CO	28.7	29.5	2.08	2.14
CH_1	48	48.2	2.35	2.28
CH_2	32 to 36	32.3 to 33.5	1.15 to 1.9	1.14 to 1.9
CO	210.1 to 211.1	210.1 to 210.7	-	-

transfer catalyst (Table 2, entry 3). The reaction is a true Wacker-type since it does not occur in the absence of copper chloride or water.

The polyketone product was characterized by infrared spectroscopy which showed the appearance of a strong carbonyl stretching band at 1720 cm^{-1}, while characteristic absorptions of the unsaturated units at 3073, 1640, and 910 cm^{-1} disappeared completely. The signals for the olefinic protons did not appear in the product. The best evidence for the oxidation of vinyl to acetyl groups was obtained from ^{13}C NMR spectroscopy, which exibits carbonyl signals at 210.1−211.1 ppm. A HETCOR 2D NMR experiment was performed to show the correlation between the hydrogen and carbon resonances. The carbon resonance at 28.7 ppm correlated with the proton at 2.08 ppm and was assigned to the methyl groups adjacent to the carbonyls, while the methine groups were identified by correlation between the carbon at 48 ppm and the proton at 2.35 ppm. However, methylene groups gave disperse satellites ranging from 32 to 36 ppm in ^{13}C NMR and from 1.15 to 1.9 ppm in ^{1}H NMR. This dispersity is due to the microtacticity of the polyketone product, which is probably atactic. All the assignments are in excellent agreement with the ^{13}C NMR[10] and ^{1}H NMR[11] data previously reported concerning the microstructures of poly(methyl vinyl ketones) (Chart 1).

Increase of the reaction temperature to 120 °C (Table 2, entry 4) and the extension of the reaction time to 44 h (Table 2, entry 5) led to overoxidation of the methyl ketone groups accompanied with other side reactions. The oxidation process was monitored by ^{13}C NMR, which showed the disappearance of the carbonyl signal at 210.1−211.1 ppm and the appearance of a new broad carbonyl signal at 170−177 ppm.

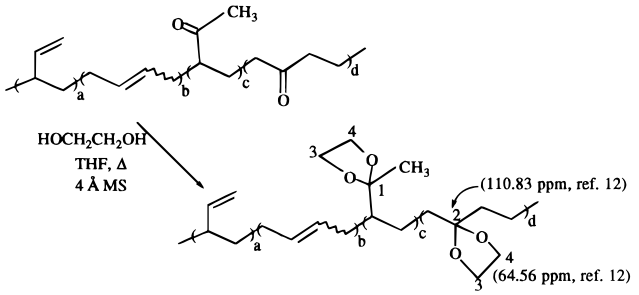
No oxidation occurred at room temperature (Table 2, entry 6), while partial conversion took place at 80 °C and under 100 psi of oxygen pressure (Table 2, entry 7). However, the product was cross-linked and was insoluble in any common solvent. The CP/MAS ^{13}C NMR shows a carbonyl signal at 209.5 ppm and the remaining olefinic carbons at 116.2 and 143.8 ppm. A carbonyl stretching band occurred at 1710 cm^{-1} in the infrared spectrum (KBr).

Table 3. Oxidation of Polybutadienes Using $PdCl_2$ (0.26 mmol), $CuCl_2 \cdot 2H_2O$ (0.26 mmol), H_2O (0.5 mL), O_2 (300 psi), and DME, 80 °C

			conversn (%)			
entry	start. polym	reacn time (h)	vinyl units	1,4-cis and trans	overall conversn (%)	polyketone no.
1	**1**	13	100		100	**4**
2[a]	**2**	17	93	80	83	**5**
3[b]	**2**	22	100	100	100	**6**
4[c]	**3**	17	93	53	61	**7**
5[b]	**3**	22	100	100	100	**8**

[a] The conversions were estimated from ^{1}H NMR using the aromatic ring as the internal standard. [b] A 0.5 mmol amount of $CuCl_2 \cdot 2H_2O$ was used. [c] The conversions were estimated from ^{1}H NMR after ketalization of the carbonyl groups.

Scheme 1



The oxidation conditions of polybutadiene **1** were optimized, and it was found that the use of only 0.26 mmol of copper chloride, instead of 2 mmol, is sufficient to lead to full conversion of vinyl groups to acetyl groups (Table 3, entry 1).

Partial conversion of polybutadienes **2** and **3** resulted when they were subjected to the same reaction conditions as **1**. In the case of **2**, the conversions were estimated by ^{1}H NMR using the aromatic ring as an internal standard (Table 3, entry 2). The overall conversion of 83% was obtained with 93% conversion of vinyl groups and 80% conversion of 1,4-units. In the case of polybutadiene **3**, the conversions were estimated after ketalization of the carbonyl groups with ethylene glycol, using the olefinic protons at 4.9 and 5.4 ppm and the ketal protons at 3.8 ppm (Table 3, entry 4). The overall conversion was 61%, with 93% conversion of vinyl groups and only 53% conversion of 1,4-units.

Characteristic signals of the ketal polymer appear in the ^{13}C NMR at 104.4 (C-1), 111.3 (C-2), and 64.7 ppm (C-3,4) (Scheme 1). These assignments are in excellent agreement with the previously reported data on ketalized alkene−carbon monoxide copolymers.[12]

When the amount of copper chloride was increased to 0.5 mmol, full conversion of the different kinds of double bonds was achieved within 22 h (Table 3, entries 3 and 5).

The average molecular weights and molecular weight polydispersities of the polymer products **4**, **6**, and **8** were determined by gel permeation chromatography. The results reported in Table 4 show that the molecular weights of the polyketones are in excellent accord with the calculated molecular weights (estimated by assuming that the degree of polymerization does not change

Table 4. Molecular Weight Averages and Polydispersities of Polyketones 4, 6, and 8

polyketone no.	M_n	M_w	M_w/M_n	calcd M_w
4	2138	3781	1.77	3413
6	2181	4146	1.9	4020
8	2639	6666	2.52	6700

during the oxidation process). The polyketone distributions (1.77−2.52) are excellent. These results confirm that no gross cross-linking or chain scission took place during the reaction.

Conclusions

The facile and complete oxidation of polybutadienes to polyketones can be achieved using catalytic amounts of palladium chloride and copper chloride. The oxidation process is sensitive to the reaction conditions, with high selectivities attained using DME as the solvent, at 80 °C and under 300 psi oxygen pressure.

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