A Novel Approach to α,β-Unsaturated Acrylated Polymers from Poly(2-methylvinylacetylene) by Homogeneous Catalysis

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ABSTRACT: Polymerization of 2-methylvinylacetylene (VA) is a selective, anion-initiated process affording poly(2-methylvinylacetylene) (PVA) with M_w of 1600−3060 and a polydispersity of 1.5−1.7. The acetylenic groups of PVA can be further functionalized by palladium(II)-catalyzed hydrocarboxylation, hydroesterification, and iodoarene/CO coupling reactions to give new polymers containing pendant functional groups of α,β-unsaturated carboxylic acids, esters, and ketones, respectively. The catalytic processes used here provide unique methods to synthesize these polymers in a stereocontrolled and stereoselective manner. Using the $Pd(OAc)_2$−dppb catalytic system, high conversions (100%) of the pendant acetylenic groups of PVA were realized, affording α,β-unsaturated acid- or ester-containing polymers with >80% selectivity at the terminal position. These polymers are not available by direct polymerization of functionalized monomers. Gel permeation chromatography indicated that neither chain scission nor cross-linking takes place during the catalytic reactions. The terminal acetylenic groups of PVA could also couple with iodoarenes and CO, in the presence of either $PdCl_2(PPh_3)_2$ or Pd-clay as the catalyst and Et_3N as base, affording branched polyketones.

Introduction

Functional polymers are generally prepared by the polymerization of monomers containing the desired functional groups. Some problems can arise with such polymerizations. For example, polycarboxylated acids are obtained by the direct polymerization of acrylic acid, or acrylic acid anhydrides, followed by hydrolysis or by the copolymerization of the acrylic acid or anhydrides with other unsaturated monomers. It is difficult to obtain the α,β-unsaturated polyacids or polyesters using these methods. This kind of α,β-unsaturated polyacid or polyester is normally more stable and less hygroscopic and shows less tendency to form cross-linked polymers than the normal polyacids or polyesters. These properties are important in some applications of polyacids, such as films and surface coating.[1] Since the catalytic hydrocarboxylation of terminal alkynes has been well developed by our group[2] and others[3] to give α,β-unsaturated acids or esters, we were interested in the possibility of preparing new kinds of α,β-unsaturated polycarboxylic acids via this method, by which the microstructure of products is easily controlled.

Polymers containing controlled degrees of functional groups are useful for custom-designed materials. Recently, much attention has been paid to preparing such polymers with functional groups by catalytic methods from polymeric precursors.[4−10] One of the most important advantages of this approach is that the functional groups of interest can be introduced in a highly selective and controllable manner. Polymers with carboxylated backbones are of particular interest, due to their potential applications. The functionalization of diene-based elastomers to give pendant polyacids has been reported in the literature.[1,4−10] Vinylacetylene is one of the industrial C-4 feed streams which is normally removed from 1,3-butadiene.[11] It is conceivable that polymerization through the vinyl group of vinylacetylene will give a new type of polymer with pendant terminal acetylenic units which will serve as a precursor to α,β-unsaturated carboxylated polymers. We now report the synthesis of a novel poly(2-methylvinylacetylene) and its functionalization by catalytic processes.

Experimental Section

Materials. 2-Methylvinylacetylene, palladium acetate ($Pd(OAc)_2$), 1,4-bis(diphenylphosphino)butane (dppb), triethylamine (Et_3N), formic acid (HCOOH), and triphenylphosphine (PPh_3) were purchased from Aldrich Chemical Co., *p*-toluenesulfonic acid (*p*-TsOH) was obtained from Fisher Scientific Co., and palladium chloride ($PdCl_2$) was 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 %; $d_{(001)}$ expansion of Pd-clay determined to be 6.7 Å),[12] and $PdCl_2(PPh_3)_2$ was prepared according to literature methods.[13] Solvents were dried and distilled prior to use. The small amount of inhibitor in 2-methylvinylacetylene must be removed by passage of the liquid monomer through a silica gel chromatography column.

Measurements. NMR spectra were recorded using a Varian Gemini 200 MHz or a Bruker 500 Hz spectrometer with an inverse detector. ^1H and ^{13}C NMR chemical shifts were measured relative to deuterated solvent peaks but were reported with reference to tetramethylsilane. A (heteronuclear multiple quantum correlation−distortionless enhancement by polarization transfer (HMQC-DEPT)) method has been used to obtain 2D heteronuclear correlation ($^{13}C-^1H$) spectra.[14] IR spectra were recorded on a Bomem MB100-C15 FTIR spectrometer with either direct film cast from a THF solution of the polymer on KBr disks or KBr film. The molecular weight averages of polymers were measured by gel permeation chromatography (GPC) using a Waters M-6000 instrument with Waters 486 UV and 410 IR detectors at 35 °C, and using tetrahydrofuran (THF) as the solvent. Polystyrene standards were used for calibration. Thermal gravimetric analyses (TGAs) were performed on Perkin Elmer equipment, and the analyses were carried out on the filaments under nitrogen. The scan rate was maintained as 10 °C/min for all samples.

Preparation of Poly(2-methylvinylacetylene) (1). Monomeric 2-methylvinylacetylene (VA; 3 mL, 2.04 g, 31 mmol) was dissolved in THF (20 mL) and cooled in a mixture of acetone−dry ice. BuLi (1.6 M, 20.3 mL) was added to the solution with stirring for 0.5 h. The color of the solution changed from light yellow to orange following the conversion

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Table 1. Polymerization of 2-Methylvinylacetylene Initiated by BuLi

entry	temp (K)	time (h)	[BuLi]/ [VA][a]	yield[b] (%)	M_W	PD[c]
1	298	2	1:1.05	95	1600	1.7
2	195	2	1:1.05	100	3060	1.5

[a] Mole ratio. [b] Isolated yield. [c] Polydispersity.

Table 2. Hydrocarboxylation of 1[a,b]

entry	temp (°C)	time (h)	[**1**]/ [cat.][c]	acid[c] (%)	conversion (%)	M_w (calcd)[e]	M_w (PD), **2** and **3**
3	110	96	100:1	200	100	5193	4367 (1.4)
4	110	12	20:1	200	100	5193	5270 (1.7)
5	110	48	20:1	5	15	3380	2700 (1.4)
6	150	6	20:1	200	100	5193	1800 (1.3)

[a] The reaction was carried out in DME (5 mL) with carbon monoxide (200 psi), HCOOH, and $\mathrm{Pd(OAc)_2}$−dppb in a 1:2 ratio. [b] Polymer **1** with M_w of 3060 and polydispersity of 1.5 was used. [c] Mole ratio. [d] By IR and ^{1}H NMR. [e] $M_w(\mathrm{calcd}) = 3060 + 2133c$ (c = % conversion of the acetylene groups).

Table 3. Hydroesterification of 1a,b

entry	temp (°C)	time (h)	[**1**]/ [cat.][c]	acid[d]	conversion (%)	M_w (calcd)[f]	M_w (PD),[c] **4** and **5**
7	110	6	50:1	*p*-TsOH	55	4590	4600 (1.5)
8	110	12	50:1	*p*-TsOH	85	5424	5360 (1.5)
9	110	24	50:1	*p*-TsOH	100	5842	5750 (1.6)
10	110	36	50:1	HCOOH	100	5842	4567 (1.4)
11	110	48	200:1	*p*-TsOH	100	5842	5290 (1.5)

[a] The reaction was carried out in DME (5 mL) with carbon monoxide (200 psi), acid (4%), and $\mathrm{Pd(OAc)_2}$−dppb in a 1:2 ratio. [b] M_w of **1** was 3060, with polydispersity of 1.5. [c] Mole ratio. [d] 4% to 1. [e] By IR and ^{1}H NMR. [f] $M_w(\mathrm{calcd}) = 3060 + 2782c$ (c = % conversion of the acetylene groups).

of all of the acetylene to its lithium salt. At this point, BuLi (0.5 mL) was added, and the orange solution was kept at −78 °C for 0.5 h and then warmed to room temperature during a period of 1.5 h. The polymerization was terminated by the addition of EtOH (95%, 3 mL), and the solution was neutralized with HCl (~8 mL, 4 N). The organic solvents were removed under vacuum, and the product was extracted with $\mathrm{CHCl_3}$, dried ($\mathrm{MgSO_4}$), and then concentrated by rotary evaporation. The ^{1}H NMR spectrum of the poly(2-methylvinylacetylene) (**1**), a sticky light yellow liquid, indicated that it was pure enough for further reactions. Analytically pure product was obtained by adding the concentrated $\mathrm{CHCl_3}$ solution of the product to pentane. The pentane layer was decanted, and the residual oil was washed with pentane twice again and dried under vacuum. ^{1}H NMR of PVA (in $\mathrm{CDCl_3}$, 200 MHz): δ 1.65 (s, 3H, $\mathrm{C}H_3$), 2.26 (s, 1H, $\mathrm{C{\equiv}C}H$), 2.08−1.74 (m, 2H, $\mathrm{C}H_2$). ^{13}C NMR (in $\mathrm{CDCl_3}$, 200 MHz): δ 30 (m, br, $C\mathrm{H_3}$), 34.2 (s, C(Me)), 55.5, 54.6, 53.6 (3s, $C\mathrm{H_2}$), 72.5 (s, $^1J_{\mathrm{HC}} = 274.4$ Hz, $\mathrm{C{\equiv}}C\mathrm{H}$), 92.0 (s, $^2J_{\mathrm{HC}} = 52.2$ Hz, $C\mathrm{{\equiv}CH}$). The assignment was confirmed by NEPT. FTIR (film): $\nu_{\mathrm{C{\equiv}C}} = 2106$ (w), $\nu_{\mathrm{{\equiv}CH}} = 3297$ (s) cm^{-1}. See Table 1 for GPC data.

Hydrocarboxylation of 1. In a typical reaction, $\mathrm{Pd(OAc)_2}$ (0.02 g, 0.09 mmol), dppb (0.07 g, 0.16 mmol), and HCOOH (0.15 g, 3.2 mmol) were added to a DME (5 mL) solution of **1** (0.1 g, 1.5 mmol) in a stainless steel autoclave (45 mL), equipped with a glass autoclave liner and a stirring bar. The autoclave was flushed with carbon monoxide three times, pressurized to 170−200 psi, closed, and heated in an oil bath preheated to the desired temperature (110 °C) for the required reaction time (24 h). The autoclave was then cooled, depressurized, and opened, and the reaction solution was evaporated to dryness. The residue was treated with NaOH (20 mL, 2 M), and the solution was filtered through Celite and then acidified with HCl (20 mL, 6 M). The precipitated polymers, **2** and **3**, were collected by filtration and dried under vacuum for 24 h. The conversion was 100% by IR. The isolated yield was 72%. ^{1}H NMR (in $\mathrm{CD_3COD}$): δ 1.5 (br, $\mathrm{C}H_2$), 1.2 (br, $\mathrm{C}H_3$), 5.5 and 6.9 (br, $\mathrm{C}H\mathrm{{=}C}H\mathrm{(COOH)}$), 5.8 and 7.2 (br, $\mathrm{C}H_2\mathrm{{=}C(COOH)}$−). ^{13}C NMR (in $\mathrm{CD_3COD}$): δ 29 (br, $\mathrm{C(}C\mathrm{H_3))}$, 32 (br, $C\mathrm{(CH_3))}$, 59.7 (br, $C\mathrm{H_2}$), 119.2 (−$C\mathrm{H{=}CH(COOH))}$, 134 ($C\mathrm{H_2{=}C(COOH)}$−), 156.0 (−$\mathrm{CH{=}}C\mathrm{H(COOH))}$, 169.9 (−$\mathrm{CH{=}CH(}C\mathrm{OOH))}$, 175.4 ($\mathrm{CH_2{=}C(}C\mathrm{OOH)}$−). This assignment was confirmed by ^{1}H−^{13}C HMQC-DEPT experiments. FTIR (KBr): $\nu_{\mathrm{C{=}O}} = 1705$ (s), $\nu_{\mathrm{COOH}} = 3400{-}2500$ (br) cm^{-1}. See Table 2 for GPC results.

Hydroesterification of 1. To an autoclave (45 mL) equipped with a stirring bar and a glass liner containing a DME (5 mL)/MeOH (2 mL) solution of 1 (0.1 g, 1.5 mmol) was added $\mathrm{Pd(OAc)_2}$ (0.01 g, 0.045 mmol), dppb (0.06 g, 0.14 mmol), and *p*-TsOH (0.012 g, 0.07 mmol). The autoclave was purged three times with CO, pressurized to 200 psi, closed, and heated in an oil bath preheated to the desired temperature (100 °C) for the required reaction time (24 h). The autoclave was then cooled, depressurized, and opened, and the solution was evaporated to dryness. The residue was dissolved in $\mathrm{Et_2O}$ and filtered, and the filtrate was concentrated by rotary evaporation to 5 mL. Pentane (15 mL) was added, and the precipitated polymer, 4 and 5, was collected by filtration and dried under vacuum for 24 h. The conversion was 100% by IR. The isolated yield was 95%. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 1.2 (br, $\mathrm{C}H_2$ and $\mathrm{C}H_3$), 3.65 (br, OMe), 5.5 and 6.8 (br, −$\mathrm{C}H\mathrm{{=}C}H\mathrm{(COOMe))}$, 5.9 and 7.4 (br, $\mathrm{C}H_2\mathrm{{=}C(COOMe)}$−). ^{13}C NMR (in $\mathrm{CDCl_3}$): δ 24.4 (br, $C\mathrm{H_3}$), 29 (br, C(Me)), 51.4 (s, $\mathrm{O}C\mathrm{H_3}$), 60.0 (br, $C\mathrm{H_2}$), 118.1 (−$C\mathrm{H{=}CH(COOMe))}$, 136 and 126 ($C\mathrm{H_2{=}}C\mathrm{(COOMe)}$−), 158.3 (−$\mathrm{CH{=}}C\mathrm{H(COOMe)}$, 166.7 (−$\mathrm{CH{=}CH(}C\mathrm{OOMe))}$, 171.2 ($\mathrm{CH_2{=}C(}C\mathrm{OOMe)}$−). IR: $\nu_{\mathrm{COMe}} = 1181$ (s), 1185 (s), $\nu_{\mathrm{C{=}CH}} = 1644$ (s), $\nu_{\mathrm{C{=}O}} = 1722$ (s) cm^{-1}. See Table 3 for GPC data.

Coupling Reaction of 1, Iodoarene, and CO. (i) Using $\mathbf{PdCl_2(PPh_3)_2}$ as the Catalyst. A mixture of **1** (0.1 g, 1.5 mmol), iodoarene (1.5 mmol), $\mathrm{Et_3N}$ (5 mL), and $\mathrm{PdCl_2(PPh_3)_2}$ (0.011 g, 0.015 mmol) was placed in an autoclave (45 mL). The autoclave was purged with carbon monoxide three times, pressurized to 600 psi, closed, and placed in an oil bath preheated to 120 °C for 12 h. The autoclave was then cooled, depressurized, and opened, mixture was filtered, and MeOH (20 mL) was added to the filtrate. The precipitated polymer, **6**, was collected by filtration, washed with MeOH (2 × 5 mL), and dried under vacuum for 24 h. The isolated yield was 95%. Spectroscopic data of **6** follow. **6a** (R = Ph). ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 1.7 (br, 5H, $\mathrm{C}H_2$ and $\mathrm{C}H_3$), 2.38 (br, $\mathrm{PhC}H_3$), 8.0−6.8 (br, 4H, Ph). ^{13}C NMR (in $\mathrm{CDCl_3}$): δ 22 (s, $\mathrm{Ph}C\mathrm{H_3}$), 29.6 (br, $C\mathrm{H_3}$), 34.5 (br, C(Me)), 54.0 (br, $C\mathrm{H_2}$), 84.0, 101 ($\equiv C$), 128.4, 129, 134, 145 (Ph), 177.5 (s, C=O). IR: $\nu_{\mathrm{C{=}O}} = 1640$ (s), $\nu_{\mathrm{C{\equiv}C}} = 2202$ (s) cm^{-1}.

6b (R = 4-MePh). ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 2.6 (br, 3H, $\mathrm{PhCH_3}$), 1.7 (br, 5H, $\mathrm{C}H_2$ and $\mathrm{CH_3}$), 8.0−6.5 (br, 4H, Ph). ^{13}C NMR (in $\mathrm{CDCl_3}$): δ 29.7 (br, −$C\mathrm{H_3}$), 34.3 (C(Me)), 54 (br, $C\mathrm{H_2}$), 84, 101 ($\equiv C$), 128.5, 129, 132.2, 144.8 (Ph), 177 (s, C=O). IR: $\nu_{\mathrm{C{=}O}} = 1640$ (s), $\nu_{\mathrm{C{\equiv}C}} = 2202$ (s) cm^{-1}.

6c (R = 4-MeOPh). ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 1.5 (br, 5H, $\mathrm{C}H_2$ and $\mathrm{CH_3}$), 3.75 (br, 3H, $\mathrm{OCH_3}$), 8.2−6.5 (br, 4H, Ph). ^{13}C NMR (in $\mathrm{CDCl_3}$): δ 35 (br, C(Me) and $C\mathrm{H_3}$), 51.8 (br, $C\mathrm{H_2}$), 85, 105 ($\equiv C$), 129.9, 137.6 (br, Ph), 175.9 (s, C=O). IR: $\nu_{\mathrm{C{=}O}} = 1650$ (s), $\nu_{\mathrm{C{\equiv}C}} = 2199.6$ (s) cm^{-1}.

6d (R = −Ph−). ^{13}C NMR (CPMAS): δ 29 (m, $C\mathrm{H_3}$), 34.6 (s, C(Me)), 52.9 ($C\mathrm{H_2}$), 53.3 (s, $\mathrm{O}C\mathrm{H_3}$), 83.8, 113.8 ($\equiv C$), 126.5, 131, 131.8, 139.2, 162, 164 (Ph), 176.7 (s, C=O). IR: $\nu_{\mathrm{C{=}O}} = 1745$ (s), $\nu_{\mathrm{C{\equiv}C}} = 2204$ (s) cm^{-1}. See Table 4 for GPC data.

(ii) Using Pd-Clay as the Catalyst. The above procedure was followed, except that Pd-clay (40 mg, 0.011 mmol) was used instead of $\mathrm{PdCl_2(PPh_3)_2}$.

Results and Discussion

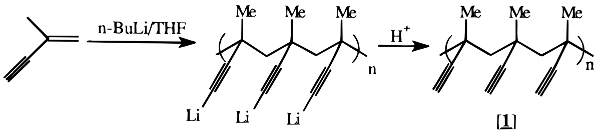
Anionic Polymerization of 2-Methylvinylacetylene and the Structure of Poly(2-methylvinylacetylene). The polymer with dangling acetylenic groups can be obtained by selectively polymerizing vinylacetylene through the vinyl group. The polymerization of vinylacetylene has been the subject of several studies.[15] Radical polymerization leads to a polymer containing both vinylic and acetylenic moieties.[16] The cationic polymerization of vinylacetylenes results in the formation of low molecular weight conjugated ladder polymers.[17] Hence, to obtain a polymer containing

Table 4. Molecular Weights and Yields of Polyketone 6[a]

compd	iodoarene	catalyst	yield[b]	M_w(calcd)[c]	M_w (PD) found
6a	iodobenzene	$PdCl_2(PPh_3)_2$	87.7	5280	5230 (1.6)
6b	4-methyliodobenzene	$PdCl_2(PPh_3)_2$	91.1	5715	5640 (1.5)
6b	4-methyliodobenzene	Pd−clay	92.5	5715	5580 (1.5)
6c	4-methoxyiodobenzene	$PdCl_2(PPh_3)_2$	90.4	6212	6100 (1.6)
6d	1,4-diiodobenzene	$PdCl_2(PPh_3)_2$	86		

[a] M_w of **1** was 2050, with polydispersity of 1.5. [b] Isolated yield. [c] M_w(calcd) = 2889 + $31M_{Ar}$ is the molecular weight of the aryl group.

exclusively triple bonds in the side chains, an anionic-initiated polymerization was performed.[15] Poly(2-methylvinylacetylene) (**1**) is readily formed by an anion-initiated polymerization in tetrahydrofuran (THF) (eq 1).[18] After substitution of the acidic acetylenic protons with lithium, the monomer was polymerized quickly to give a red-orange solution, apparently in its lithium salt form. The reprotonation of the formed polymer with acid (HCl, 4 N) led to the desired poly(2-methylvinylacetylene) (**1**). GPC measurements showed that the average molecular weight of the polymer (M_w) varied from 1600 to 3060, with the polydispersity of 1.5−1.7, depending on the reaction conditions. The polymer of higher molecular weight was obtained by polymerization at lower temperature (−78 °C) (see Table 1, entry 2).



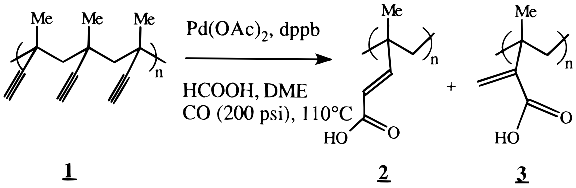
(1)

There are no vinyl proton resonances in either the ^1H or the ^{13}C NMR spectrum of the product; hence, we concluded that the possibility of the polymerization occurring through acetylenic moieties is excluded. The acetylenic proton resonance at 2.26 ppm and the carbon resonances at 72.5 and 92.0 ppm clearly indicate the presence of the pendant terminal acetylene unit. An intense $\nu_{\equiv CH}$ stretching band at 3297 cm^{-1} and C≡C stretching band at 2106 cm^{-1} in the IR spectrum (film) of **1** further confirmed the presence of the acetylenic group. Therefore, the polymer has a saturated backbone with pendant triple bonds in each unit, as shown in eq 1.

However, the anion-initiated polymerization of 2-methylvinylacetylene is not regioselective. ^{13}C NMR spectroscopy of **1** showed three resonances of CH_2 (55.5, 54.6, 53.6 ppm) and a broad resonance of *C*(Me) (34.2 ppm), corresponding to three types of connections of monomer, head−tail, head−head, and tail−tail, in a 1:1:1 ratio, clearly demonstrating its random combination. The lack of regioselectivity of the polymerization was probably due to the existence of an anionic acetylenic group. The anionic acetylenic group diminished the stabilization effect of the methyl group to the anion center and led to polymerization in a nonregioselective manner.

As an anion-initiatized reaction, the polymerization stops once the vinyl sites become hindered. For example, 1-ethynylcyclohexene, a more hindered vinylacetylene derivative, cannot be polymerized by this method. As a result of the significant stability difference of the anion of styrene and 2-methylvinylacetylene, the copolymerization of styrene and 2-methylvinylacetylene does not occur, and only PVA and polystyrene (PS) were obtained by this method.

Catalytic Hydrocarboxylation of PVA. A wide variety of different catalyst systems have been reported for the hydrocarboxylation of terminal acetylene derivatives.[19] A well-developed catalytic system using $Pd(OAc)_2$ and 1,4-bis(diphenylphosphino)butane (dppb) in the presence of formic acid is able to convert terminal acetylene derivatives to α,*β*-unsaturated acids in excellent yields with high regioselectivity.[2a] The selectivity for carboxylation at the nonterminal position of the acetylenic group was over 90% using this catalyst system.[2a] In view of its reactivity, with terminal acetylenic groups dangling, **1** is an appropriate polymeric precursor for modification to access desired α,*β*-unsaturated polymeric derivatives. Thus, the hydrocarboxylation of **1** using carbon monoxide and formic acid in the presence of $Pd(OAc)_2$ and dppb as the cocatalyst, in DME for 24 h, afforded α,*β*-unsaturated polyacids **2** and **3** (eq 2).



(2)

The hydrocarboxylation reaction was monitored by IR during the course of the reaction. A decrease of the intensities of $\nu_{C\equiv C}$ at 2200 cm^{-1} and $\nu_{\equiv CH}$ at 3200 cm^{-1} and increase of the intensity of $\nu_{C=O}$ at 1720 cm^{-1} was observed. The hydrocarboxylation process was considered completed when both $\nu_{C\equiv C}$ at 2200 cm^{-1} and $\nu_{\equiv CH}$ at 3200 cm^{-1} of the acetylenic group could not be observed by FTIR.

Studies indicate that the properties of terminal acetylene groups of **1** are similar to normal small terminal acetylene compounds, and the best reaction conditions to convert them into α,*β*-unsaturated acids are the same as those reported for monomeric analysis of this group.[2a] The required reaction time is proportional to the substrate/catalyst ratio for complete conversion (Table 2, entries 3 and 4). The acid seems to have a significant influence on the efficiency of the catalytic reaction. Very low conversion was obtained in the presence of a catalytic amount of formic acid (Table 2, entry 5). Less than a 1:1 ratio of substrate and formic acid will also lead to much longer reaction times, chain scission, and low conversion rates (entry 5). The catalyst efficiency in the polymeric system is a little less than that in small molecule systems. Six mole percentage of Pd(II) catalyst is necessary to effect complete conversion under moderate temperature (110 °C) and pressure (~200 psi) in a reasonable length of time (24 h) (entry 4). Although higher reaction temperatures will shorten the reaction time, chain scission occurs (entry 6).

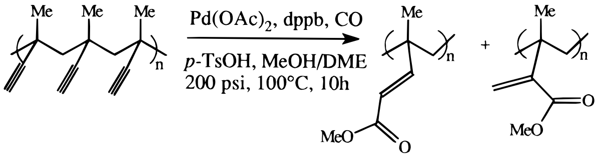
There were no absorptions for acetylenic groups in the IR spectra of **2** and **3** (i.e.,) at 2106 and 3297 cm^{-1}), while a broad stretching absorption for the hydroxyl groups occurred at 3650−2500 cm^{-1}, as did an intense carbonyl stretching band at 1705 cm^{-1}. The molecular weight of this α,*β*-unsaturated polyacid **2** and **3**, determined by GPC, is 5270 (Table 2, entry 4), which is close to the calculated molecular weight (5193). The molecular weight distribution of 1.7 indicated little cross-linking or chain scission under these conditions and high selective conversion of hydrocarboxylation with no obvious side reactions. Therefore, complete hydrocarboxylation of the acetylenic groups in **1** did occur.

As expected, the α,β-unsaturated polyacid is fairly stable. TGA measurements of a mixture of **2** and **3** showed that they decompose at 320 °C or above. The structures of **2** and **3** were characterized by spectroscopic methods. A $^1H-^{13}C$ heteronuclear correlation obtained by using HMQC-DEPT techniques showed that the formed polyesters contain both CH and $H_2C=$ moieties, indicating that the polyacids **2** and **3** are carbonylated at the terminal and nonterminal positions of the acetylenic group, respectively. The CH proton resonances at 5.5 and 6.9 ppm are correlated to the two carbon resonances at 156.0 and 119.2 ppm. The ^{13}C NMR spectrum exhibits *two* broad carbonyl signals at 169.9 and 175.4 ppm, which correspond to the linear (**2**) and the branched (**3**) polymers. It is known that the carbonyl resonance of *trans*-$Bu^tCH=CHCOOH$ in the ^{13}C NMR is at 166 ppm, whereas the carbonyl resonance of $CH_2=C(Me)COOH$ is at 173.1 ppm.[2a,20] Therefore, the resonance at 169.9 ppm is assigned to the linear isomer **2**, and that at 175.4 ppm is assigned to the branched isomer **3** The integration of the two resonances in the ^{13}C NMR spectrum was determined by *inverse gated decoupling*, indicating that the ratio of linear to branch isomers is 4:1. The ratio of linear to branched isomers obtained in the hydrocarboxylation of $Bu^tC\equiv CH$ under similar reaction conditions is 79:21, consistent with our observations.[2a]

At this stage, we cannot determine the ratio of cis and trans isomers of *linear* carboxylated product **2** because of the large line-broadening in both the ^1H and ^{13}C NMR spectra of **2**. Since the branched acetylenic group of PVA is structurally similar to $Bu^tC\equiv CH$ carrying a very bulky group, and it is known that hydrocarboxylation of $Bu^tC\equiv CH$ at similar reaction conditions gave only trans- isomer of the terminal carboxylated product, the trans isomer of the terminal carboxylated product **2** is expected to be major isomer in the case of polymers.[2a]

A cross-linked polymer with ν_{COOH} at 3500−2500 cm^{-1} and ν_{CO} at 1700 cm^{-1} was formed under oxidative carbonylation conditions using palladium chloride and cupric chloride as catalysts and CO (1 atm) and O_2 (1 atm) in THF (15 mL) and HCl (concentrated, 1 mL) at room temperature.[21] The cross-linking is believed to occur through coupling of the terminal acetylenic groups catalyzed by Cu(II)/O_2.

Catalytic Hydroesterification of PVA. The hydroesterification of terminal acetylene derivatives catalyzed by transition metal complexes has been the subject of several studies.[3c,8,9b] Based on the hydrocarbonylation conditions discussed above, we anticipated that the hydroesterification reaction should take place under similar reaction conditions. Indeed, by using the Pd(OAc)$_2$/dppb catalytic system in the presence of *p*-TsOH and MeOH in DME for 24 h, complete hydroesterification of **1** was achieved, affording new α,β-unsaturated polyesters **4** and **5** (eq 3). In accord with the hydrocarbonylation process, the intensity of the characteristic absorption bands attributed to the pendant acetylenic groups at 3297 and 2106 cm^{-1} decrease, while there is an increase in the methoxycarbonyl group bands appearing at 1722, 1185, and 1181 cm^{-1}. The conversion of the acetylenic units to methoxycarbonyl groups increased with increasing reaction time and temperature (Table 3, entries 7−9). Full conversion of **1** to the methyl polyesters was achieved at 110 °C in 24 h (entry 9). Although both HCOOH and *p*-TsOH are effective acids for the catalytic hydroesterification of **1**, *p*-TsOH is more efficient than HCOOH (Table 3, entry 9). A slight chain scission also was observed when HCOOH was used as the acid (entry 10). Although the total catalytic turnovers can be increased, the reaction time becomes much longer (Table 3, entry 11).

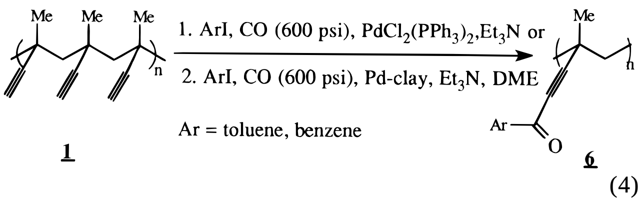


(3)

The polyesters **4** and **5** are very soluble in most organic solvents. The molecular weights of the resulting polymers were determined by GPC in THF. The molecular weight of the polyester (5750) is quite close to the calculated molecular weight (5842), and the similar polydispersity of the starting polymer and product indicated that no cross-linking or chain scission occurred in the catalytic process (Table 3, entry 9).

The structure of the polyesters (**4** and **5**) and the selectivity for the hydroesterification of PVA were also investigated by spectroscopic methods. No characteristic resonances of the acetylenic group in the ^1H and ^{13}C NMR spectra were observed, indicating complete conversion of the acetylenic groups of **1**. The ^1H and ^{13}C NMR resonance patterns of **4** and **5** are similar to those of polyacids **2** and **3**, showing the same regioselectivity in both hydrocarbonylation and hydroesterification. The resonance of the methyl protons of the methoxy group appeared at 3.65 ppm in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, the resonance at 51.4 ppm is assigned to the methoxy carbon. There are two types of carbonyl signals at 171.2 and 166.7 ppm in the ^{13}C NMR spectrum. Following the reasoning in the polyacid case, the resonance at 171.2 ppm is due to the branched isomer, while that at 166.7 ppm is attributed to the linear isomer. Gate-decoupled ^{13}C NMR of **4** and **5** studies indicated that two types of carbonyl groups at 171.2 and 166.7 ppm are in a 1:5 ratio. Thus, the ratio of the linear isomer to branched isomer is estimated as 1:5. We conclude that both hydrocarboxylation and hydroesterification of PVA showed good selectivity toward introduction of a carbonyl group onto the terminal carbon of the pendant acetylene group, and the ratio of linear to branch isomers is close to ~4:1.

Coupling Reaction of Poly(vinylacetylene) with ArI and CO. The coupling reaction of iodoarenes, CO, and terminal acetylenes is a useful method in organic chemistry for the synthesis of α,β-unsaturated ketones.[22−24] Coupling of **1** with iodoarenes and CO, catalyzed by $PdCl_2(PPh_3)_2$ in the presence of dppb in THF/Et_3N (5:2), afforded α,β-unsaturated polyketone **6**. The IR spectra of **6** showed the disappearance of the vibration characteristic of acetylenic units at 3297 cm^{-1} and the appearance of an intense carbonyl stretching band at 1645 cm^{-1}. The adsorption band of $C\equiv C$ shifted from 2104 to 2200 cm^{-1}, corresponding to a nonterminal triple-bond formation. The resulting polyketone showed only one carbonyl resonance, at 175 ppm, in the ^{13}C NMR spectrum, indicating that the carbonyl group is attached to the terminal carbon atom of the pendant acetylenic unit.[23] Therefore, the polyketone **6** obtained under these conditions has linear-type pendant groups (eq 4).

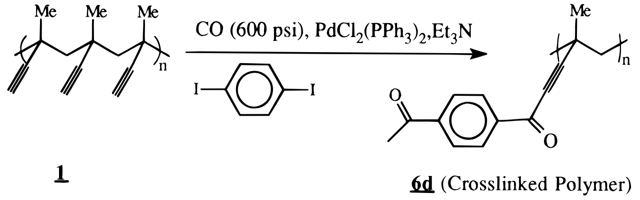


(4)

The molecular weight of these α,β-unsaturated polyketones, determined by GPC, is close to the calculated molecular weights. The detailed measurements are listed in Table 4. The α,β-unsaturated polyketones are fairly stable, and decomposition of the polyketone **6a** occurred at 320 °C, with 74% of its weight lost at 500°C (TGA).

Prior work in our laboratory has shown that the anchoring of palladium to a clay can generate an effective catalytic system for several reactions, such as the reductive carbonylation of nitro compounds to urethanes,[23] the oxidative carbonylation of amines,[24] and the hydroesterification of olefins[25]. When montmorillonite(bipyridine)palladium acetate (Pd-clay) was used as catalyst instead of PdCl$_2$(PPh$_3$)$_2$ in the coupling reaction of iodoarene−CO and **1**, the same results were obtained, to give α,β-unsaturated polyketone **6b** (eq 4). The molecular weight of this unsaturated polyketone was 5580, similar with that obtained before.

When difunctional 1,4-diiodobenzene was used as a coupling reagent, a purple cross-linked polyketone resin **6d** was obtained (eq 5). Solid state ^{13}C NMR indicated the presence of the CO at 170 ppm. An FTIR spectrum also confirmed the existence of adsorption bands at 1645 and 2204 cm^{-1}. Since the peaks are fairly broad, the possibility of coupling between PVA and iodoarene cannot be ruled out.[26,27]



(5)

The polyketone **6d** is a spongelike material with decomposition beginning at 300 °C, and 60% of the mass still remained even at 600 °C, indicated by TGA measurements.

Conclusions

The novel polymer, poly(2-methylvinylacetylene) (**1**), obtained by an anionic-initiated polymerization selectively through the vinyl group, can be converted into α,β-unsaturated polyacids, polyesters, or polyketones using Pd(II)-catalyzed processes in a controllable manner. The catalytic processes described herein constitute simple and novel methods for the synthesis of unsaturated polyacids, esters, and ketones, not available by the direct polymerization of functionalized monomers.

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