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SYNTHESIS AND POLYMERIZATION OF THE ORGANOMETALLIC MONOMER SERIES BASED ON CYMANTRENYLETHYL ACRYLATE

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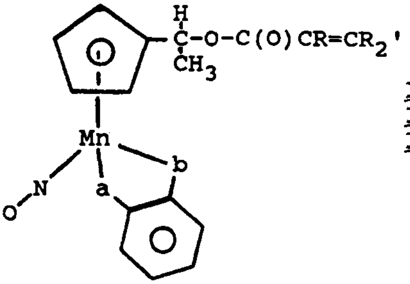
ABSTRACT

$\{\eta^5-C_5H_4[CH(CH_3)OC(O)CH{=}CH_2]\}Mn(CO)_3$, $\{\eta^5-C_5H_4[CH(CH_3)OC(O)C(CH_3){=}CH_2]\}Mn(CO)_3$, and $\{\eta^5-C_5H_4[CH(CH_3)OC(O)CH{=}C(CH_3)_2]\}Mn(CO)_3$ were synthesized (63, 57, and 51%, respectively) from $\{\eta^5-C_5H_4[CH(CH_3)OH]\}Mn(CO)_3$, toluenesulfonic acid, and the acrylic, methacrylic, and dimethylacrylic acids, and from $\{\eta^5\text{-}C_5H_4[CH(CH_3)OH]\}Mn(CO)_3$, pyridine, and the acrylic, methacrylic, and dimethylacrylic acyl chlorides [26, 48, and 25% (impure), respectively]. No product was obtained when NaH was used as the base in the latter method. The acrylate and methacrylate monomers were bulk homopolymerized at 65°C with AIBN (75% yield, M_n = 88,550 g/mol; 78% yield, M_n = 349,350 g/mol, respectively). The dimethylacrylate did not polymerize under these conditions. The polymers lost vinylcymantrene upon heating to 257 and 279°C, respectively. The polymers did not exhibit a clear T_g but were observed to soften at 85 and 160°C, respectively, and they could be pulled into fibers.

INTRODUCTION

Interest in organometallic monomers and polymers has grown [1–17] since vinylferrocene was first polymerized in 1955 [18]. When organometallic molecules are polymerized or copolymerized with organic monomers, they provide materials which have increased rigidity or stability when compared to pure organic polymers, they can be converted to ceramics, they prove useful in the preparation of silicon chips, they contain catalytic centers, and they may be electroactive [1, 2, 19, 21].

Efforts to make a new electroactive organometallic polymer based on *I* have been made by our group [22].



		R	R'
Ia	=	H	H
Ib	=	CH_3	H
Ic	=	H	CH_3

Ia–Ic were chosen for study due to the interesting characteristics and reversible redox phenomena exhibited by compounds containing metallacyclic rings [23, 24], like MnS_2C_2. It was expected that partially reduced or oxidized polymers resulting from *I* would show semiconductivity [21].

A scheme to synthesize type *I* compounds from their corresponding cymantrenylethyl acrylate (*IIa, IIc*) or methacrylate (*IIb*) is being pursued [25, 26] in our lab. Syntheses of the intermediates *IIa–IIc* from 1-cymantrenylethanol and the appropriate acrylate or methacrylate bearing reactant have been completed (see Fig. 1). Esterification with acrylic acids and toluenesulfonic acid catalyst (Route 1), acrylic chlorides and pyridine (Route 2) and acrylic chlorides and sodium hydride (Route 3) have been used successfully in the past (see Table 1) to prepare acrylate and methacrylate monomers. We report here the results of our studies using all three routes to prepare *IIa–IIc*.

In addition, the results of the free radical polymerization of *IIa–IIc* are described.

EXPERIMENTAL AND RESULTS

Chemicals

CH_2Cl_2, $CH_2{=}CHCO_2H$, $CH_2{=}C(CH_3)CO_2H$ (98.5%), $(CH_3)_2C{=}CHCO_2H$ (97%), Silica gel (Grade 62, 60–200 mesh, 140Å; when

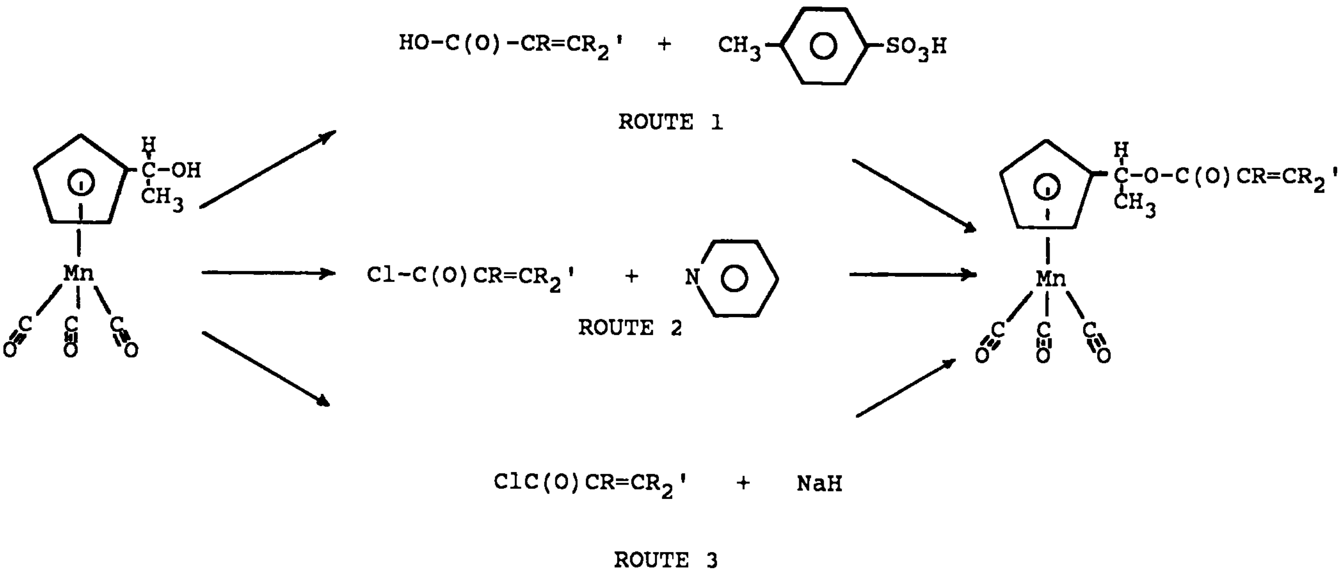


FIG. 1. Synthesis of 1-cymantrenylethyl acrylates. *IIa*: R = H, R′ = H. *IIb*: R = CH_3, R′ = H. *IIc*: R = H, R′ = CH_3.

TABLE 1. Results of Previous Esterifications[a]

Route	Compound	Yield, %	Ref.
1	$\{\eta^5\text{-}C_5H_4[CH_2OC(O)CH{=}CH]\}(\eta^5\text{-}C_5H_5)Fe$	85.0	11
	$\{\eta^6\text{-}C_6H_5[CH_2OC(O)CH{=}CH_2]\}Cr(CO)_3$	0	27
2	$\{\eta^5\text{-}C_5H_4[CH_2OC(O)CH{=}CH_2]\}(\eta^5\text{-}C_5H_5)Fe$	75.0	11
	$\{\eta^5\text{-}C_5H_4[CH_2OC(O)C(CH_3){=}CH_2]\}(\eta^5\text{-}C_5H_5)Fe$	85.0	11
	$\{\eta^5\text{-}C_5H_4[CH_2CH_2OC(O)CH{=}CH_2]\}(\eta^5\text{-}C_5H_5)Fe$	65.7	12
	$\{\eta^5\text{-}C_5H_4[CH_2CH_2OC(O)C(CH_3){=}CH_2]\}(\eta^5\text{-}C_5H_5)Fe$	81.0	12
	$\{\eta^5\text{-}C_5H_4[CH(CH_3)OC(O)CH{=}CH_2]\}(\eta^5\text{-}C_5H_5)Fe$	62.0	12
	$\{\eta^5\text{-}C_6H_5[CH_2CH_2OC(O)CH{=}CH_2]\}Cr(CO)_3$	34.0,56.3[b]	13
	$\{\eta^6\text{-}C_6H_5[CH_2CH_2OC(O)C(CH_3){=}CH_2]\}Cr(CO)_3$	57.6	28
	$\{\eta^6\text{-}C_6H_5[CH_2OC(O)CH{=}CH_2]\}Cr(CO)_3$	51.4	27
	(η^4-2,4-Hexadienyl-2-yl acrylate)-tricarbonyl iron	62.5	29
	(η^4-2,4-Hexadienyl-2-yl methacrylate)-tricarbonyl iron	62.0	30
	$\{\eta^5\text{-}C_5H_4[CH(CH_3)OC(O)CH{=}CH_2]\}Co(CO)_2$	26.0	31
	$\{\eta^5\text{-}C_5H_4[CH_2OC(O)CH{=}CH_2]\}Co(CO)_2$	35.0	31
3	$\{\eta^5\text{-}C_5H_4[CH_2OC(O)CH{=}CH_2]\}Co(CO)_2$	56.0	31

[a] See Fig. 1 for route descriptions.

[b] Ether and benzene, respectively, as reaction solvents.

indicated, was activated by heating for 4 h at 180°C), NaH (60% dispersion in mineral oil), $H_2C{=}CHC(O)Cl$, $H_2C{=}C(CH_3)C(O)Cl$, and $(CH_3)_2C{=}CHC(O)Cl$ (98, 90, and 97%, respectively, all vacuum distilled prior to use) were purchased from Aldrich and used as is unless otherwise noted. Na_2SO_4 and Na_2CO_3 (ACS reagent grade, anhydrous), hydroquinone, hexane, benzene, THF (dried over sodium/benzophenone and distilled prior to use), and pyridine (vacuum distilled prior to use) were purchased from Fisher Scientific and used as is unless otherwise noted. Toluenesulfonic acid was obtained from Matheson, Coleman and Bell and used without further purification. AIBN was obtained from Kodak Chemical Company and recrystallized three times in CH_3OH before use (CH_3OH was obtained from Anachemia Chemicals and dried for at least 24 h with Na_2SO_4 before use). $\{\eta^5\text{-}C_5H_4[CH(CH_3)OH]\}Mn(CO)_3$(*III*) was synthesized using standard literature methods [2b, 3, 7, 8, 33–36].

Instrumentation

All ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ with TMS as an internal standard using a Varian VXR-300 spectrometer and 300 and 75.4 MHz frequencies, respectively. IR's were recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were performed by Oneida Research Services. A Perkin-Elmer DSC-1B and a Perkin-Elmer TGS-Z equipped with Systems 4 Microprocessor Controller and Data Station System were used for thermal analyses. A Fisher-Jones Melting Point Apparatus was used to study the softening points. GPC's were recorded using a Waters Liquid Chromatograph equipped with a R401 Differential Refractometer Model 600A Solvent Delivery System, Model U6A Universal LC Injector, and 10^4 and 10^5 Å I-Styragel polystyrene columns connected in series. The GPC was operated at room temperature using THF as a solvent. Linear polystyrene standards were used in the GPC analyses in conjunction with the universal calibration method to determine the molecular weights of the polymers [36]. The intrinsic viscosities of the polymers were determined by using a Cannon-Fenske A96K size 50 viscometer at 25 ± 0.01°C, using THF as the solvent. The polystyrene intrinsic viscosities were determined by using literature data [37].

Syntheses of Monomers *IIa–IIc*

All syntheses and manipulations were performed under N_2 while maintaining exposure to light to a minimum.

$\{\eta^5-C_5H_4[CH(CH_3)OC(O)CH=CH_2]\}Mn(CO)_3$, *IIa*

Route 1. $\{\eta^5-C_5H_4[CH(OH)CH_3]\}Mn(CO)_3$ (1.00 g, 4.03 mmol, *III*), *p*-$CH_3C_6H_4-SO_3H \cdot H_2O$ (8.0 mg, 0.042 mmol), $C_6H_4(OH)_2$ (8.0 mg, 0.073 mmol), $CH_2=CHCO_2H$ (1.45 g, 20.12 mmol), and CH_2Cl_2 (30 mL) were refluxed for 5 h. The yellow solution was then cooled with an ice bath and treated with aqueous Na_2CO_3 (20%, 25 mL). The organic layer was separated, washed with H_2O (5 ×, 25 mL portions), dried over Na_2SO_4, filtered, and the CH_2Cl_2 was removed at reduced pressure and 35°C. The resultant yellow liquid was chromatographed on a column of activated silica gel (1″ × 6″, preeluted with C_6H_{14}) and initially developed with C_6H_{14} until a first yellow band separated. The column was then eluted with CH_2Cl_2/C_6H_{14} (1/2) and then CH_2Cl_2/C_6H_{14} (1/1). The first yellow band was collected and identified as vinylcymantrene (*IV*) (*vide infra*). The first 25% of the second yellow band was collected and yielded mostly *bis*-cymantrenylethyl ether (*V*). The remaining 75% of the second yellow band was collected and the solvent removed at reduced pressure and 35°C. The resultant waxy oil was taken up in acetone and gravity filtered. The filtrate was evaporated to dryness under vacuum to produce *IIa* as a clear yellow oil (0.84 g, 2.87 mmol, 69%: average yield 63% for three separate syntheses). (See Fig. 2 for numbering scheme; shifts in ppm.)

^1H NMR: 6.45 (dd, 1, $J_{6,7}$ = 1.2 Hz, $J_{6,5}$ = 17.3 Hz, H_6); 6.14 (m, 1, $J_{5,6}$ = 17.3 Hz, $J_{5,7}$ = 10.3 Hz, H_5); 5.87 (dd, 1, $J_{7,6}$ = 1.2 Hz, $J_{7,5}$ = 10.3 Hz, H_7); 5.73 (q, 1, $J_{3,4}$ = 6.3 Hz, H_3); 4.90 (dd, 2, H_2 and H_2'); 4.65 (s, 2, H_1 and H_1'); 1.50 (d, 3, $J_{4,3}$ = 6.6 Hz, H_4).

$^{13}C\{^1H\}$ NMR (see Fig. 2 for numbering scheme, shifts in ppm): 225 (C_1); 165 (C_7); 131 (C_8); 128 (C_9); 84 and 83 (C_2 and C_2'); 81 (C_3 and C_3'); 66 (C_5); 20 (C_6).

IR (neat, cm^{-1}: 2030 and 1935 (A^1 and E modes of inorganic CO); 1735 (ester CO); 1640 and 1620 (C=C).

Elemental analysis (theoretical/found): %H, 3.67/3.73; %C, 51.67/51.60.

Route 2. III (0.90 g, 3.63 mmol), C_6H_6 (50 mL) and pyridine (0.54 g, 6.81 mmol) were cooled with an ice bath while stirring. $CH_2=CHC(O)Cl$ (0.69 g, 7.63 mmol) in C_6H_6 (0.5 mL) was added dropwise over a period of 15 min. Additional C_6H_6 (20 mL) was added through the dropping funnel and the slurry was warmed to 25°C and stirred for 5 h. The slurry was filtered and the yellow filtrate was washed with $NaHCO_3/NaCl$ (5%/5%, 3 × with 25 mL portions). The organic layer was separated, dried

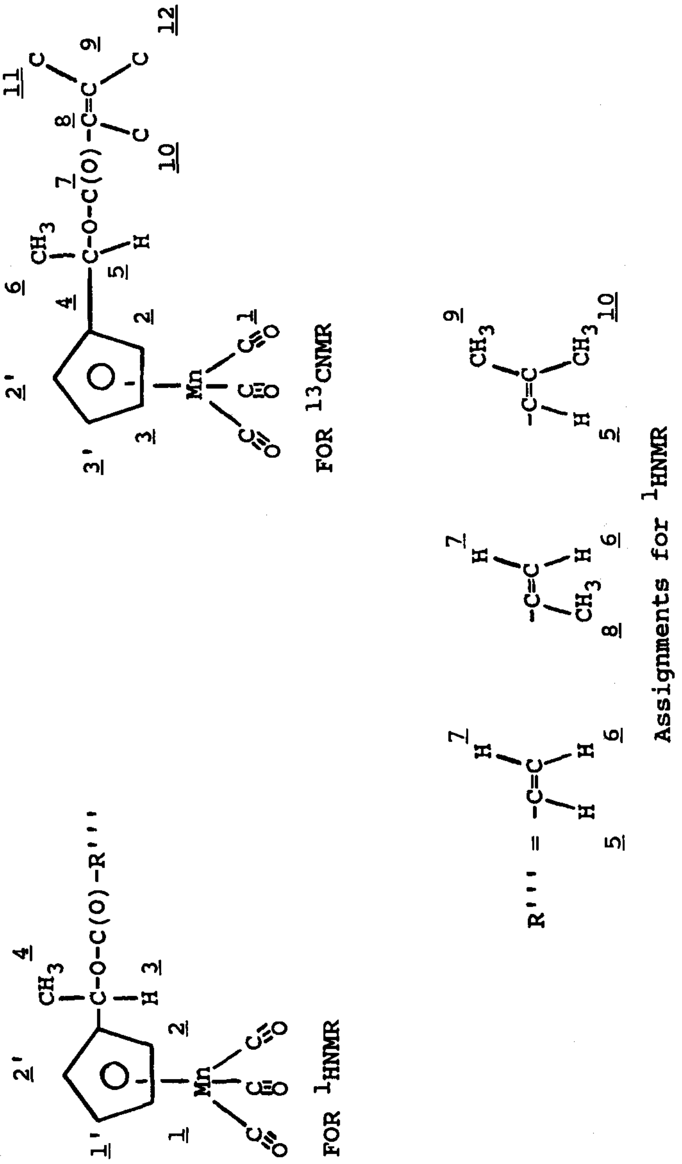


FIG. 2. Numbering scheme for ¹H- and ¹³C-NMR spectral identification [22].

with Na_2SO_4, filtered, and the solvent removed under reduced pressure at 35°C. The resultant yellow oil was chromatographed on silica gel (1′ × 7″, preeluted with C_6H_6) using C_6H_6 developer. The first yellow band yielded *IIa* (0.25 g, 0.83 mmol, 23%: average yield 26% for 8 separate syntheses) using techniques described above.

Route 3. NaH (0.18 g of dispersion, 7.50 mmol) and THF (30 mL) were cooled with stirring using a dry ice/acetone bath. *III* (1.00 g, 4.03 mmol) and $CH_2{=}CHC(O)Cl$ (0.425 g, 4.70 mmol) were added and the yellow solution was refluxed for 3 h. After cooling to 25°C, the reaction mixture was stirred for 13 additional hours. Only unreacted *III* and other noncharacterizable materials were recovered.

$\{\eta^5{-}C_5H_4[CH(CH_3)OC(O)C(CH_3){=}CH_2]\}Mn(CO)_3$, *IIb*

Route 1. IIb was obtained (57% average yield of three runs) as a clear yellow oil using the same procedure used for *IIa* Route 1 above, except that $CH_2{=}C(CH_3)CO_2H$ was substituted for $CH_2{=}CHCO_2H$.

^1H NMR: 6.17 (s, 1, H_6); 5.72 (d, 1, $J_{3,4}$ = 6.3 Hz, H_3); 5.60 (s, 1, H_7); 4.88 (d, 2, H_2 and H_2'); 4.65 (s, 2, H_1 and H_1'); 1.96 (s, 3, H_8); 1.49(d, 3, $J_{4,3}$ = 6.3 Hz, H_4). $^{13}C\{^1H\}$ NMR: 225 (C_1); 166 (C_7); 136 (C_8); 126 (C_9; 105 (C_4); 84 and 83 (C_2 and C_2'); 81.5 and 81.0 (C_3 and C_3'); 66 (C_5); 21 and 18 (C_{10} and C_6).

IR (neat); 2030 and 1935 (A^1 and E modes); 1725 (ester CO); 1640 (C=C).

Elemental analysis (theoretical/found): %H, 4.14/4.09; %C, 53.18/53.23.

Route 2. IIb was obtained (48% average yield of 6 syntheses) using a procedure similar to that used for *IIa* Route 2 except $CH_2{=}C(CH_3)C(O)Cl$ was used in place of $CH_2CHC(O)Cl$.

$\{\eta^5{-}C_5H_4[CH(CH_3)OC(O)CH{=}C(CH_3)_2]\}Mn(CO)_3$, *IIc*

Route 1. IIc was obtained (51% average of two syntheses) as a clear yellow oil using a procedure similar to that used for *IIa* Route 1 except $(CH_3)_2C{=}CHCO_2H$ was used in place of $CH_2{=}CHCO_2H$. In addition, a longer chromatographic column (1″ × 10″) was required.

^1H NMR: 5.68 (m, 2, H_3 and H_5; 4.88 (dd, 2, H_2 and H_2'); 4.63 (t, 2, H_1 and H_1') 2.18 (d, 3, J = 10 Hz H_9); 1.90 (s, 3, H_{10}), 1.46 (d, 3, $J_{4,3}$ = 6.6 Hz, H_4).

$^{13}C\{^1H\}$ NMR: 225 (C_1); 166 (C_7); 158 (C_8); 116 (C_9); 105 (C_4); 84 and 83 (C_2 and C_2'); 81.5 and 81 (C_3 and C_3'); 65 (C_5); 27 (C_{12}); 21 and 20 (C_6 and C_{11}).

IR (neat): 2030 and 1930 (A^1 and E modes); 1720 (ester CO); 1650 (C=C).

Elemental analysis (theoretical/found): %H, 4.58/4.55; %C, 54.56/54.54.

Route 2. IIc was obtained using a procedure similar to that used for *IIa* Route 2 except $C(CH_3)_2{=}CC(O)Cl$ was used in place of $CH_2{=}CHC(O)Cl$. Pure samples of *IIc* could not be obtained by using this method.

Bulk Homopolymerization Studies

Polymerization of IIa

IIa (1.0068 g, 3.33 mmol) and AIBN (0.005 g, 0.030 mmol) were heated for 17 h at 65°C in a sealed Schlenk tube. The tube was degassed [3–15 min freeze (0°C)-thaw cycles] prior to heating. The hard yellow polymer (*IIap*) was dissolved in THF and precipitated from stirring C_6H_{14} three times. The light yellow, powdery solid was dried under vacuum until a constant mass was obtained (0.93 g, 95% yield: 78% was the average yield for 2 runs). M_n was 88,550 h/mol. [ỹ] was 172. IR(KBr): 2030 and 1930 (A^1 and E modes); 1730 (ester CO).

TGA: 76% average mass loss at 257°C and 92% loss at 519°C. DSC indicated decomposition at 255–265°C. Visual inspection of the polymer while heating indicated a softening point of about 85°C.

Polymerization of IIb

IIb was polymerized to *IIbp* by using the same procedure as that for *IIa*. The average yield was 78% for two runs. M_n was 349,350 g/mol. [ỹ] was 183. IR (KBR): 2030 and 1935 (A^1 and E modes); 1735 (ester CO).

TGA: 75% mass loss at 279°C and a 92% loss at 421°C. DSC indicated decomposition at 266–275°C. Visual inspection of the polymer while heating indicated a softening point of 160°C.

Polymerization of IIc

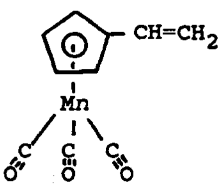
Repeated attempts to polymerize *IIc* by using the procedure above failed to yield polymer.

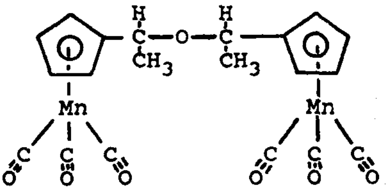
RESULTS AND DISCUSSION

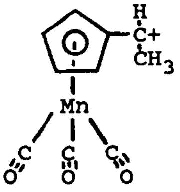
Synthesis of Monomers

The best route to *IIa–IIc* based on yield and ease of preparation appears to be Route 1. Route 2 requires prior distillation of the acyl chlorides and pyridine, gives lower yields, and produces other unidentified impurities which were difficult to separate from the products. Since Route 3 did not yield any product after two attempts with *III* and $CH_2{=}CHC(O)Cl$, it was not pursued.

In the use of Route 2, *IV* and *V* were found in small quantities in all cases. *V* has been found previously in the *p*-toluenesulfonic acid catalyzed dehydration of *III* [35]. Both *IV* and *V* probably result from the formation of the carbocation *VI* which either loses a proton from the α-methyl to form *IV* or attacks another molecule of *III* to form the protonated form of *V*. Both *IV* and *V* were identified by their characteristic ^1H NMR and IR [35].


IV


V


VI

It is interesting to note that a white waxlike material was found in all of the yellow oils after chromatographic purification. This material, which was insoluble in acetone, was easily separated from *IIa–IIc* in the final purification step. The ^1H NMR of the impurity revealed two broadened peaks at 1.3 and 0.9 ppm in a ratio of 2 : 1 respectively. Comparison of the spectra to standard hydrocarbon spectra indicates the impurity to be a hydrocarbon. The same impurity is also found in the product obtained from chromatographic purification of 1-cymantrenyl-ethanol. Formation of this impurity by catalytic assistance of the metal complexes is currently under study.

Monomer Spectroscopy

The ^1H-NMR and ^{13}C-NMR resonances were assigned by comparison of the spectra with literature data.

The Cp proton resonances for *IIa–IIc* appear slightly downfield from those for vinylcymantrene [3]. The downfield shift is caused by the greater deshielding effect of the ester linkage over the vinyl group. The Cp carbon resonances agree with those trends found for substituted cymantrene compounds such as 2-cymantrenyl-2-butanol [38] and methyl- and ethyl-cymantrene. The nonequivalence of the Cp carbons when a chiral center is attached to the ring has been noted previously [39, 40].

The proton and carbon shifts and resonance patterns for the alkene fragments in *IIa–IIc* agree with those for methylacrylate, methyl methacrylate, and 3, 3-dimethylacrylic acid [41], respectively. The H_3 proton is greatly deshielded due to the combined influences of the adjacent Cp and ester groups [31] while the C_5 resonance is close to that of the α-carbon in 1-ferrocenyl ethanol [40].

Polymer Studies

The polymers *IIap* and *IIbp* have been prepared by using bulk polymerization while past studies have used solution polymerization exclusively [2b]. *IIc* did not polymerize under the conditions used here, probably because of steric crowding around the double bond. The yield of polymers obtained compare well with yields of other organometallic acrylate polymerizations [11–13, 28, 29, 42–44]. DSC characterization was performed on *IIap* and *IIbp* from 25–300°C but no T_g transitions could be discerned. However, visual inspection of the polymer during heating on a hot stage revealed that the polymers became soft (85°C for *IIap* and 185°C for *IIbp*) and could be pulled into fibers (160°C for *IIap* and 200°C for *IIbp*). These softening points are higher than those found for vinylcymantrene [28].

DSC and TGA both indicate decomposition of the polymers in the 255 to 270°C range. The average 75% weight loss indicated by TGA for *IIap* and *IIbp* is consistent with loss of vinylcymantrene. Trapping and subsequent ^1H NMR characterization of the volatile product from the decomposition of *IIap* have shown it to be vinylcymantrene. It should be noted that in the attempted free radical polymerization of 1-ferrocenylethyl acrylate at 70–90°C, only vinylferrocene and acrylic acid were found [12]. In addition, similar decompositions have been found for poly-*t*-butyl methacrylate and other esters above 250°C [45].

It should be noted that *IIap* yielded a binodal GPC curve while *IIbp* did not. In order to have enough material to perform GPC analysis and intrinsic viscosity measurements on *IIap*, the yields of two separate polymerizations were combined. GPC and viscosity measurements were performed on the composite, and the average GPC weight of the two nodes was used for molecular weight calculations. It is possible that both polymerizations of *IIa* resulted in identical binodal distributions. However, it is also possible that oven temperature variations between the two runs of *IIa* may have resulted in two different weight distributions which appear binodal when combined.

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