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Ruthenium complex catalyzed polymerization of OH or COOH group containing alkynes to give functionalized poly(acetylene)s

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Abstract

The ruthenium(III) complex $[(Cp^*)RuCl_2]_2$ (Cp^* = permethylcyclopentadienyl) catalyzes polymerization of propiolic acid to give a mixture of poly(propiolic acid), $[-CH{=}C(COOH)-]_n$ (**1**), and cyclic trimers, 1,2,4- and 1,3,5-benzenetricarboxylic acids. GPC analysis shows *MN* and *MW* values of the polymer of 4.0×10^3 and 4.3×10^3, respectively. Reaction of propiolic acid in the presence of the Ru(II) complex, $(Cp^*)RuCl(L)$ (L = 1,5-cyclooctadiene and norbornadiene), gives the cyclic trimers rather than **1**. $[(Cp^*)RuCl_2]_2$ catalyzes polymerization of acetylenedicarboxylic acid and of propargyl alcohol to give the corresponding poly(acetylene) derivatives, $[-C(COOH){=}C(COOH)-]_n$ (**2**) and $[-CH{=}C(CH_2OH)-]_n$ (**3**), respectively. Polymerization of ethyl propiolate, 2-butyn-1,4-diol, phenylacetylene and (trimethylsilyl)acetylene using $[(Cp^*)RuCl_2]_2$ gives the corresponding polymers $[-CH{=}C(COOEt)-]_n$ (**4**), $[-C(CH_2OH){=}C(CH_2OH)-]_n$ (**5**), $[-CH{=}CPh-]_n$ (**6**) and $[-CH{=}C(SiMe_3)-]_n$ (**7**) in low yields.

Key words: Catalysis; Polymerization; Polyacetylene; Ruthenium complexes; Cyclopentadienyl complexes; Halide complexes

Introduction

Polymerization of substituted acetylenes provides a useful tool for the synthesis of various poly(acetylene) derivatives which have potential utility as electrical and optoelectric materials [1, 2] and as materials for gas separation [3–5]. The substituted poly(acetylene)s are practically more useful because of their higher stability toward air and their higher solubility in organic solvents compared to non-substituted poly(acetylene) [6]. Previous studies have revealed that several transition metal compounds such as $MoCl_5$, WCl_6 and $Mo(O)Cl_5$ catalyze effective polymerization of phenylacetylene and of 1-alkynes to give the corresponding substituted poly(acetylene)s in the presence of co-catalysts such as organotin and organoaluminum compounds [7, 8]. Very recently W(0) complexes have been reported to catalyze substituted alkynes without a co-catalyst [9]. Late transition metal complexes such as $[RhCl(diene)]_2$, $RuCl_3$ and $PdCl_2$ also catalyze the polymerization of substituted alkynes [10–12]. There have been fewer reports on transition metal complex catalyzed polymerization of OH or COOH containing alkynes to give the corresponding poly(acetylene) derivatives [13] although the polymers would be of use as water soluble poly(acetylene) derivatives or could be converted to chemically modified polymer materials by alkylation or acylation of the OH groups in the polymer molecule. In the course of our study on the polymerization of organic substrates catalyzed by transition metal complexes [14] we have observed polymerization of several substituted alkynes catalyzed by organoruthenium complexes which were reported to promote oligomerization or polymerization of unsaturated molecules such as alkynes, alkenes, and also cycloalkenes [15–17]. Here we report the polymerization of CH_2OH or COOH group containing alkynes by using Ru complexes, as well as characterization of the polymers.

Experimental

General procedures, materials and measurement

All manipulations of the complexes and polymerization were carried out under nitrogen or argon using standard Schlenk technique. Solvents were dried by the usual method, distilled and stored under nitrogen. $[(Cp^*)RuCl_2]_2$ (Cp^* = permethylcyclopentadienyl),

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[(Cp*)RuClL] (L = PPh_3, 1,5-cyclooctadiene, norbornadiene) and $Pd_2(dba)_3$ (dba = dibenzylidene acetone) were prepared according to the literature methods [18, 19]. The monomers were purchased and distilled under reduced pressure prior to use except for acetylenedicarboxylic acid which was used as received. IR spectra were recorded on a Jasco IR 810 spectrophotometer. UV–Vis spectra were obtained with a Jasco Ubest-35 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Jeol EX-90 or GX-500 spectrometers. Elemental analyses were carried on a Yanagimoto type MT-2 CHN autocorder. GPC analyses were carried out on a Toso HLC-8020 using a DMF solution of LiBr (0.01 M) as the eluent and polystyrene as the standard.

Polymerization of propiolic acid catalyzed by [(Cp)RuCl$_2$]$_2$*

To a toluene (10 ml) solution of [(Cp*)$RuCl_2$]$_2$ (42 mg, 0.14 mmol Ru) was added propiolic acid (340 mg, 4.9 mmol) at room temperature. The reaction mixture was heated at 100 °C for 14 h with stirring to give a brown solid as the product. The formed solid was filtered, washed with toluene several times and dried *in vacuo* to give the product as a brown powdery solid (250 mg, 73%). ^1H NMR and GPC analyses of the product showed that it contained $[-CH{=}C(COOH)-]_n$ (**1**), 1,2,4- and 1,3,5-benzenetricarboxylic acids in a 75:9:16 ration. *Anal.* Found: C, 51.4; H, 3.6. Calc. for $(C_3H_2O_2)_n$: C, 51.4; H, 2.9%.

Cyclotrimerization of propiolic acid catalyzed by [(Cp)RuCl(cod)] and by [(Cp*)RuCl(nbd)]*

To a toluene (5 ml) solution of [(Cp*)RuCl(cod)] (cod = 1,5-cyclooctadiene) (34 mg, 0.090 mmol Ru) was added propiolic acid (320 mg, 4.6 mmol) at room temperature. The reaction mixture was heated at 60 °C for 13 h with stirring. The brown precipitate that formed was filtered, washed with toluene several times and dried *in vacuo* to give a mixture of 1,2,4- and 1,3,5-benzenetricarboxylic acids (180 mg, 56%). *Anal.* Found: C, 51.7; H, 3.5. Calc. for $(C_3H_2O_2)_3$: C, 51.4; H, 2.9%. The ^1H NMR spectrum of the product shows the product ratio of 1,2,4- to 1,3,5- as 43:57.

Reaction in DME (1,2-dimethoxyethane) and reaction catalyzed by [(Cp*)RuCl(nbd)] (nbd = norbornadiene) were carried out analogously.

Polymerization of propiolic acid catalyzed by Pd$_2$(dba)$_3$

To a toluene (*c*. 10 ml) solution of $Pd_2(dba)_3$ (57 mg, 0.12 mmol Pd) was added propiolic acid (280 mg, 4.0 mmol) at room temperature. Heating the black reaction mixture for 15 h at 100 °C causes deposition of a dark brown solid which was filtered, washed with toluene and dried *in vacuo* (140 mg, 50%). The product was revealed as a mixture of poly(propiolic acid) (**1**) and 1,2,4- and 1,3,5-benzenetricarboxylic acid.

Polymerization of acetylenedicarboxylic acid catalyzed by [(Cp)RuCl$_2$]$_2$*

To a THF (10 ml) solution of [(Cp*)$RuCl_2$]$_2$ (24 mg, 0.078 mmol Ru) was added acetylenedicarboxylic acid (440 mg, 3.9 mmol) at room temperature. The reaction mixture was heated at 70 °C for 14 h with stirring. After removal of the solvent under reduced pressure the resulting brown powder was dissolved in benzene (*c*. 200 ml). The polymer product was extracted with water from the benzene layer. Evaporation of the water layer gave $[-C(COOH){=}C(COOH)-]_n$ (**2**) as a brown solid which was purified by reprecipitation from acetone–hexane (290 mg, 66%). *Anal.* Found: C, 41.3; H, 2.4. Calc. for $(C_4H_2O_4)_n$: C, 42.1; H, 1.8%.

Polymerization of propargyl alcohol catalyzed by [(Cp)RuCl$_2$]$_2$*

To a toluene (10 ml) solution of [(Cp*)$RuCl_2$]$_2$ (25 mg, 0.081 mmol Ru) was added propargyl alcohol (230 mg, 4.1 mmol) at room temperature. The reaction mixture was heated at 100 °C for 12 h with stirring. Removal of the solvent under reduced pressure followed by repeated washing of the brown oily product with Et_2O gave $[-CH{=}C(CH_2OH)-]_n$ (**3**) as a dark brown solid (140 mg, 61%). *Anal.* Found: C, 66.4; H, 6.3. Calc. for $(C_3H_4O)_n$: C, 64.3; H, 7.2%.

Polymerization of ethyl propiolate catalyzed by [(Cp)RuCl$_2$]$_2$*

To a toluene (10 ml) solution of [(Cp*)$RuCl_2$]$_2$ (39 mg, 0.13 mmol Ru) was added ethyl propiolate (450 mg, 4.6 mmol) at room temperature. The reaction mixture was heated at 100 °C for 14 h with stirring to give a small amount of black solid which was filtered, washed with toluene and dried *in vacuo* to give $[-CH{=}C(COOEt)-]_n$ (**4**) as a black solid (49 mg, 11%). Satisfactory analytical results were not obtained probably due to contamination with metal compounds in the product.

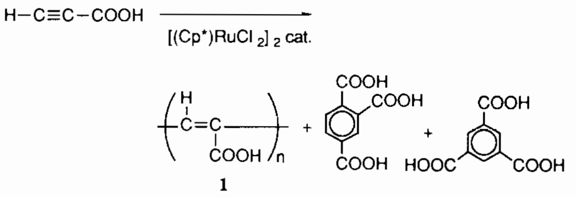
Polymerization of 2-butyn-1,4-diol catalyzed by [(Cp)RuCl$_2$]$_2$*

To a THF (10 ml) solution of [(Cp*)$RuCl_2$]$_2$ (110 mg, 0.36 mmol Ru) was added 2-butyn-1,4-diol (1.93 g, 22 mmol) at room temperature. The reaction mixture was heated at 70 °C for 16 h with stirring. The resulting brown solution was poured into Et_2O (*c*. 200 ml) to give $[-C(CH_2OH){=}C(CH_2OH)-]_n$ (**5**) as a dark brown solid which was filtered and dried *in vacuo* (190 mg, 10%). *Anal.* Found: C, 52.6; H, 6.7. Calc. for $(C_4H_6O_2)_n$: C, 55.8; H, 7.0%.

Results and discussion

Polymerization and cyclotrimerization of propiolic acid

Reaction of propiolic acid in the presence of a catalytic amount of $[(Cp^*)RuCl_2]_2$ at 100 °C gives a brown powdery product which is separated from the reaction mixture. The product is soluble in water, MeOH and acetone, and sparingly soluble in $CHCl_3$. Elemental analysis agrees with the formula $(C_3H_2O_2)_n$, and spectroscopic and GPC measurements indicate that the product is a mixture of poly(propiolic acid), $[-CH{=}C(COOH)-]_n$ (**1**) and smaller amounts of 1,2,4- and 1,3,5-benzenetricarboxylic acids.



(1)

The IR spectrum of the product (Fig. 1(a)) shows a ν(C=O) vibration peak at 1700 cm^{-1} accompanied by a shoulder peak at 1600 cm^{-1} which is assigned to the ν(C=C) vibration. The peaks due to ν(C−H) (3320 cm^{-1}) and ν(C≡C) (2150 cm^{-1}) vibrations of the C≡CH group of the monomer or of polymer terminal structure are almost negligible. The presence of a broad peak around 3000 cm^{-1} due to the ν(O−H) band excludes the other possible structures for the polymer, $[-CH{=}CH-COO-]_n$ or $[-C({=}CH_2)-COO-]_n$, that would be formed through Ru complex catalyzed polyaddition of carboxylic acid to the C≡C triple bond [14, 20]. Figure 2(a) shows GPC curves of the product giving two peaks. Retention time of the later peak agrees with that of 1,2,4- and 1,3,5-benzenetricarboxylic acids (Fig. 2(b)), while the earlier peak corresponds to molecular weights of $MN = 4.0 \times 10^3$ and $MW = 4.3 \times 10^3$ based on polystyrene standard. The ^{1}H NMR spectrum of the product in DMSO-d_6 shows peaks due to 1,2,4-benzenetricarboxylic acid (multiplet at 8.2–7.7 ppm) and the 1,3,5-isomer (singlet at 8.6 ppm) in a 35:65 peak area ratio although peaks due to the vinyl hydrogens of **1** are almost negligible. Most of the already reported poly(acetylene) derivatives were reported to show broadened ^{1}H NMR peaks or no peaks partly due to disordered structures and due to partial oxidation of the polymer chain. Poly(aryl acetylene)s prepared by Rh(I) complex catalyzed polymerization of the corresponding alkynes give sharp ^{1}H

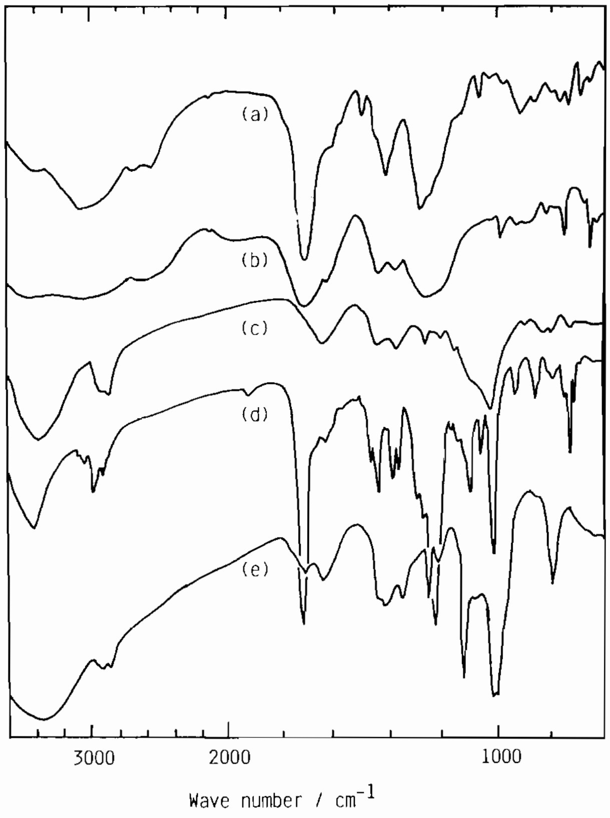


Fig. 1. IR spectra of: (a) $[-CH{=}C(COOH)-]_n$ (**1**), (b) $[-C(COOH){=}C(COOH)-]_n$ (**2**), (c) $[-CH{=}C(CH_2OH)-]_n$ (**3**), (d) $[-CH{=}C(COOEt)-]_n$ (**4**), (e) $[-C(CH_2OH){=}C(CH_2OH)-]_n$ (**5**). Polymer **1** contains the cyclotrimerization products, see text.

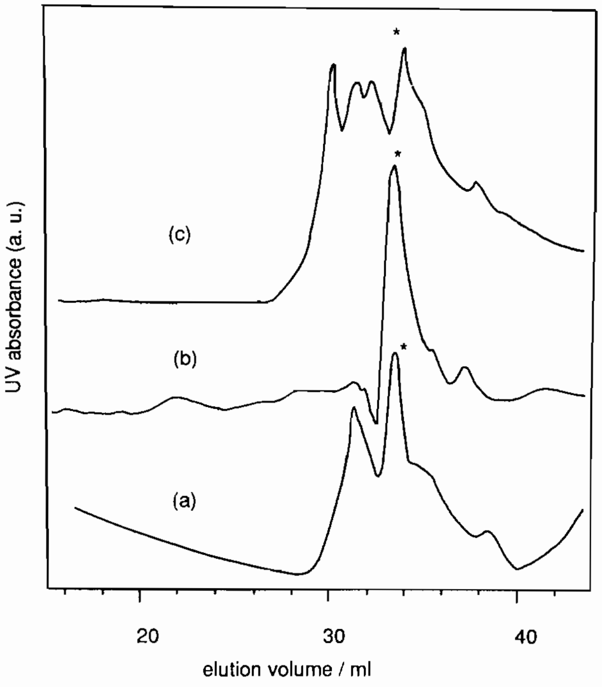


Fig. 2. GPC traces of: (a) $[-CH{=}C(COOH)-]_n$ (**1**) prepared by $[(Cp^*)RuCl_2]_2$ catalyzed polymerization of propiolic acid, (b) 1,2,4-benzenetricarboxylic acid, (c) $[-CH{=}C(COOH)-]_n$ (**1**) prepared by $Pd_2(dba)_3$ catalyzed polymerization of propiolic acid. The peak marked by an asterisk in (a) is due to the cyclic trimers.

NMR peaks owing to the well regulated polymer structures including *cis–trans* conformations of the monomer units [10, 11]. Since polymer **1** obtained from reaction (1) shows no ^1H NMR peaks it is not feasible to determine the *cis–trans* structure of the monomer units of the polymer unambiguously. The ratio of **1** and the cyclic trimers in the product is determined as 75:25 by comparison of the ^1H NMR peak area of the trimers with that of dioxane added in the NMR sample as the internal standard. Thus, the ratio among **1**, 1,2,4-benzenetricarboxylic acid and the 1,3,5-isomer is shown to be 75:9:16. The UV–Vis spectrum of **1** shows a peak due to a $\pi\pi^*$ transition at 320 nm that is higher than that of monomer (*c.* 270 nm), suggesting the presence of a poly(acetylene) main chain structure involving elongated π-conjugation. Separation of polymer **1** from the cyclic trimers by reprecipitation is not feasible due to the similar solubility of the compounds.

The Pd(0) complex, $Pd_2(dba)_3$ (dba = dibenzylidene acetone), also catalyzes polymerization of propiolic acid to give a brown powdery product which is a mixture of polymer **1** and the cyclic trimers based on a comparison of the IR and ^1H NMR peaks and the GPC curves with those of the product in reaction (1). The GPC curve of the product (Fig. 2(c)) is more complicated than that of the product in reaction (1).

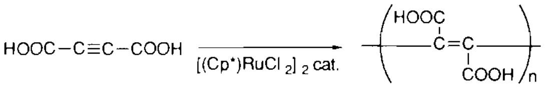
Polymerization of propiolic acid has been reported to proceed under γ-ray irradiation [21] or in the presence of a transition metal catalyst such as $MoCl_5$–$SnPh_4$ and $RuCl_3$ [13], although the polymer yields are significantly lower than reaction (1) (27% and 11%, respectively). IR peak positions of the polymer in the present study agree with that obtained by the $MoCl_5$–$SnPh_4$ catalyzed reaction. The similarity of the IR spectrum of the product in reaction (1) containing **1** and cyclic trimers to that of **1** by the Mo catalyst is probably due to similar peak positions between **1** and the cyclic trimers. The intrinsic viscosity of the product of reaction (1) in DMF solution is 0.057 dl g^{-1}, while poly(propiolic acid) **1** by the $MoCl_5$–$SnBu_4$ catalyst shows a somewhat lower intrinsic viscosity (0.045 dl g^{-1}) [13].

Heating propiolic acid in the presence of Ru(II) complexes with a diene ligand, [(Cp*)RuCl(L)] (L = 1,5-cyclooctadiene, norbornadiene), gives a mixture of 1,2,4- and 1,3,5-benzenetricarboxylic acids. Formation of polymer **1** is not observed in the reaction. The ratio among the isomers changes depending on the solvent and the diene ligand used. The [(Cp*)RuCl(cod)] catalyzed reaction gives the 1,2,4- and 1,3,5-benzenetricarboxylic acids in a ratio of 74:26 in DME and of 43:57 in toluene, respectively, although the reaction catalyzed by the nbd coordinated complex gives the product ratios of 57:43 in DME and of 43:57 in toluene, respectively.

The above reactions of propiolic acid catalyzed by Ru(III), Ru(II) and Pd(0) complexes give the products in different ratios depending on the catalyst. The $[(Cp^*)RuCl_2]_2$ catalyzed reaction gives polymer **1** with a simple GPC pattern although the product contains cyclic trimers of the alkyne. [(Cp*)RuCl(diene)] catalyzes cyclotrimerization of propiolic acid rather than polymerization. The $Pd_2(dba)_3$ catalyzed reaction gives polymer **1** as the main product although it shows several peaks in the GPC curve. Transition metal catalyzed polymerization and cyclotrimerization of alkynes seem to proceed through different pathways. Several reports on the mechanism of cobalt complex catalyzed cyclotrimerization of alkynes revealed that the reaction involves a metallacycle as the intermediate [22, 23]. On the other hand, polymerization of alkynes is generally accepted to proceed through successive insertion of a C≡C triple bond into the metal–carbon bond of the active species of the reaction or through metathesis polymerization of the alkynes. Reaction (1) in the present study seems to have two separate reaction pathways of propiolic acid to give the polymer or the cyclic trimer depending on the structures of the active species. The simple GPC pattern of the product in reaction (1) suggests that the active species for polymerization is single, while another active species which is responsible for the cyclotrimerization exists in the reaction mixture. The $Pd_2(dba)_3$ catalyst gives several structures of active species which are responsible for formation of polymers with several molecular weights.

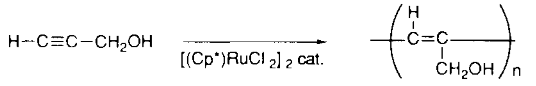
Polymerization of other alkynes

Table 1 summarizes the results of polymerization of other substituted alkynes catalyzed by the Ru complex. Acetylenedicarboxylic acid and propargyl alcohol polymerize in the presence of the $[(Cp^*)RuCl_2]_2$ catalyst to give the polymers $[-C(COOH){=}C(COOH)-]_n$ (**2**) and $[-CH{=}C(CH_2OH)-]_n$ (**3**), respectively.



$$HOOC-C{\equiv}C-COOH \xrightarrow[{[(Cp^*)RuCl_2]_2\ cat.}]{} \left(\overset{HOOC}{C}{=}\underset{COOH}{C}\right)_n \qquad (2)$$

2



$$H-C{\equiv}C-CH_2OH \xrightarrow[{[(Cp^*)RuCl_2]_2\ cat.}]{} \left(\overset{H}{C}{=}\underset{CH_2OH}{C}\right)_n \qquad (3)$$

3

$MoCl_5$ was reported to catalyze polymerization of acetylenedicarboxylic acid in the presence of $SnPh_4$ to give **2** in lower yield [12]. The IR spectrum of **2** obtained in the present study is identical with that prepared by the Mo catalyst. The ^1H NMR spectrum of **2** in DMSO-d_6 shows a peak due to the OH hydrogens at 12.6 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows two peaks at 167 and 133 ppm which are assigned to the C=O and C=C carbons, respectively. It is not feasible to determine the *cis–trans* structure of the polymers from the NMR

TABLE 1. Polymerization of substituted alkynes catalyzed by $[(Cp^*)RuCl_2]_2$

Monomer	Conditions	Polymer			
		No.	Yield (%)	*MN* ($\times 10^{-3}$)	*MW* ($\times 10^{-3}$)
$HC{\equiv}C{-}COOH$	toluene, 100 °C, 14 h	**1**	74[b]	4.0	4.3
$HOOC{-}C{\equiv}C{-}COOH$	THF, 70 °C, 14 h	**2**	65	[c]	[c]
$HC{\equiv}C{-}CH_2OH$	THF, 70 °C, 14 h	**3**	60	[d]	[d]
$HC{\equiv}C{-}COOEt$	toluene, 100 °C, 14 h	**4**	11	[e]	[e]
$HOCH_2{-}C{\equiv}C{-}CH_2OH$	THF, 70 °C, 16 h	**5**	10	14	19

[a] Determined by GPC in DMF solutions (0.01 M LiBr) based on polystyrene standard. [b] Product contains cyclic trimer. Molecular weights excluding the trimer part are shown. [c] Very wide molecular weight distribution is observed. See Fig. 3. [d] Not measured due to low solubility of the polymer. [e] GPC curves show complicated pattern.

or IR spectra. The product in reaction (3) is completely soluble in DMSO although benzenehexacarboxylic acid is not soluble in the solvent, indicating that the product of reaction (3) contains a cyclotrimerization product in almost negligible amount, unlike in reaction (1). The molecular weight distribution of **2** is very wide as observed from the GPC results (Fig. 3). The IR spectrum of **3** shows peaks due to the ν(C=C) vibration at 1640 cm^{-1} as well as peaks due to ν(O–H) (3700–3100 cm^{-1}) and ν(C–H) (2910 and 2850 cm^{-1}) vibrations. The IR data and elemental analysis agree with the polymer structure. NMR and GPC measurements are not feasible due to the poor solubility of the polymer toward organic solvents. The IR peak positions of **3** in the present study agree with that prepared by the $MoCl_5$ catalyzed reaction [6].

Ethyl ester of propiolic acid gives the corresponding polymers $[-CH{=}C(COOEt){-}]_n$ (**4**). The mixture after reaction for 14 h contains considerable amounts of the monomer unreacted and the cyclic trimers as revealed by GPC and NMR measurements of the reaction solution. Polymerization of the ester seems to be much slower than that of propiolic acid under similar conditions. Monosubstituted acetylene without an OH or COOH group such as phenylacetylene and (trimethylsilyl)acetylene undergoes polymerization to give the corresponding polymers in lower yields and molecular weights than the polymers by the already reported Mo, W and Rh catalysts. Diphenylacetylene, diethyl acetylenedicarboxylate, *m*-ethynylbenzoic acid and 1-hexyne do not give polymerization products nor cyclotrimerization products under similar conditions.

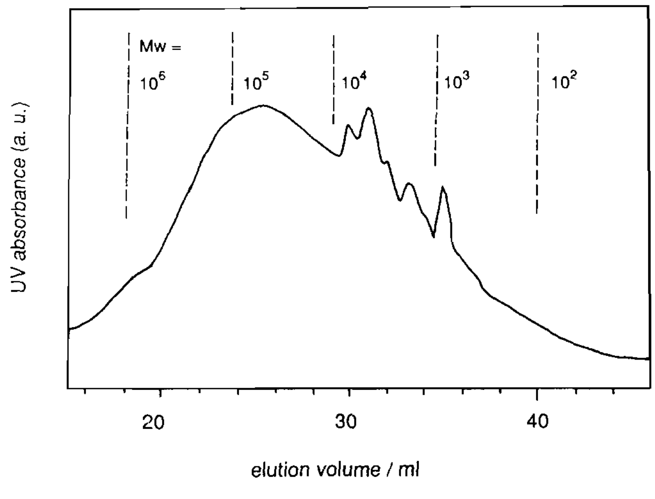


Fig. 3. GPC traces of $[-C(COOH){=}C(COOH){-}]_n$ (**2**). Standard positions of *MW* values based on polystyrene standard are shown by dotted lines.

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