Preparation of Novel Poly(enol ester)s by Ruthenium Complex Catalyzed Polyaddition of Dicarboxylic Acids with Diynes

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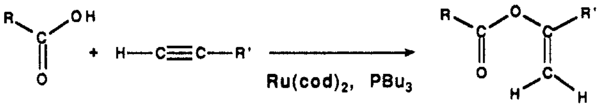
ABSTRACT: Terephthalic acid reacts with 1,7-octadiyne in the presence of a catalytic amount of $Ru(cod)_2$ (cod = 1,5-η^5-cyclooctadienyl), PBu_3, and maleic anhydride in DMF (*N,N*-dimethylformamide) to give a poly(enol ester), $[OCO—C_6H_4—COO—C(=CH_2)—C_4H_8—C(=CH_2)]_n$ (1), through Markovnikov addition of the OH group to the C≡C triple bond. The ^1H and ^{13}C NMR spectra show the signals due to the vinylidene group (=CH_2) whose position and splitting pattern agree with those of a model compound, PhCOO—C(=CH_2)—C_4H_8—C(=CH_2)—OCOPh, prepared from similar reaction of benzoic acid with 1,7-octadiyne. GPC analysis of the polymer shows M_n and M_w values of 6.6×10^3 and 1.1×10^4, respectively. A similar reaction without PBu_3 gives a polymer containing both vinylidene (C=CH_2) and vinylene (-CH=CH-) groups in the molecule. Polyaddition of acetylenedicarboxylic acid with 1,4-diethynylbenzene using $Ru(cod)_2$ catalyst gives a poly(enol ester), $[OCO—C≡C—COO—C(=CH_2)—C_6H_4—C(=CH_2)]_n$ (2). Polyaddition of terephthalic acid with 1,4-diethynylbenzene in the presence of $Ru(cod)_2—PBu_3$ catalyst gives the polymer product which has poor solubility in organic solvents. The structure of the polymer is determined as $[OCO—C_6H_4—COO—CH=CH—C_6H_4—CH=CH-]_n$ (3), having a vinylene group, on the basis of the ^1H NMR spectrum of the DMSO (dimethyl sulfoxide) soluble part of the product ($M_n = 1.6 \times 10^3$ and $M_w = 4.7 \times 10^3$, respectively). TG analysis of 1 shows a sharp weight loss up to 50% in a range 275–350 °C, while 2 and 3 undergo a more gradual weight loss in wider temperature ranges.

Introduction

Polymer synthesis using organotransition metal complexes as catalyst has achieved remarkable progress recently.[1] In particular, various bond formation processes involving the reaction of two kinds of functional groups catalyzed by the metal complexes have been applied to the polymerization reaction of bifunctional organic compounds to give novel polyesters and polyamides and the related polymers.[2] Application of the bond forming reactions using the soluble catalyst[3] to polyaddition and polycondensation of the organic substrates will provide the novel polymers that would hardly be obtained from the conventional polymerization procedure.

Recently, Mitsudo and Watanabe's group and Dixneuf's group have reported that Ru complexes catalyze addition of carboxylic acid to 1-alkyne to give enol ester under mild conditions.[4,5] This reaction proceeds in the presence of PBu_3 through Markovnikov addition of the -COOH group to the C≡C triple bond to give the enol ester having the vinylidene (C=CH_2) structure (eq 1), while the reaction in the absence of PBu_3 gives the other regioisomer with the vinylene (-CH=CH-) group as the main product. The $Ru(cod)_2$-PBu_3 catalyzed reaction of dicarboxylic acids with diynes would give poly(enol ester)s having a vinylidene group through polyaddition with regioselectivity of Markovnikov addition according to Scheme 1. The polymer molecule is expected to undergo functionalization by facile H—O, H—S, H—Si bond addition to the vinylidene group or cross-linking caused by addition of radical or cation species to initiate polymerization of the olefin group. On the other hand, there have been few reports on the polymers with vinylidene groups except for poly(allene)s[6] and poly(ketene)s.[7] These observations prompted us to apply the above addition of the COOH group to alkynes catalyzed by the Ru complex to polymer synthesis. Here we report results of Ru complex catalyzed polyaddition of several dicarboxylic acids with diynes to give novel poly(enol ester)s and the structure and the properties of the polymers.



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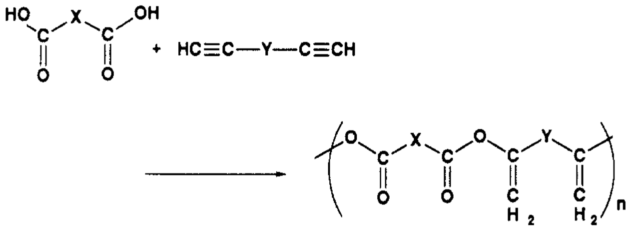
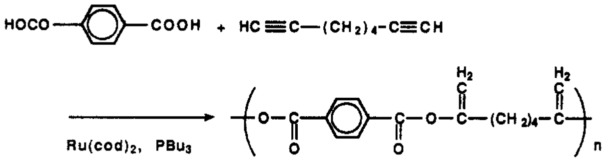
Scheme 1



Results and Discussion

Polyaddition of Terephthalic Acid with 1,7-Octadiyne. An equimolar reaction of terephthalic acid with 1,7-octadiyne in the presence of catalytic amounts of $Ru(cod)_2$ (cod = 1,5-η^5-cyclooctadienyl), PBu_3, and maleic anhydride in DMF (*N,N*-dimethylformamide) gives a poly(enol ester), $[OCO—C_6H_4—COO—C(=CH_2)—C_4H_8—C(=CH_2)]_n$ (1), as a brown solid in 28% yield. Although benzene and toluene, which have been used as the solvent of the Ru complex catalyzed addition of carboxylic acid to 1-alkyne,[4,5] are not appropriate to the above polyaddition due to the low solubility of terephthalic acid in the nonpolar solvents, the polyaddition proceeds smoothly in polar



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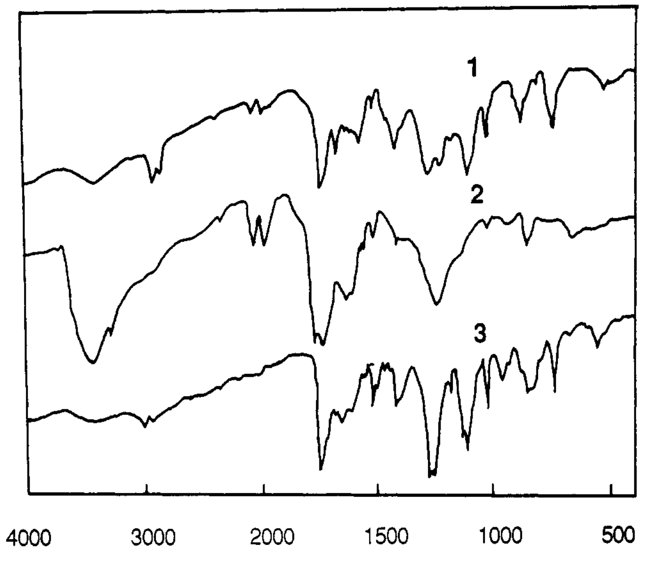


Figure 1. IR spectra of 1–3 in KBr disks.

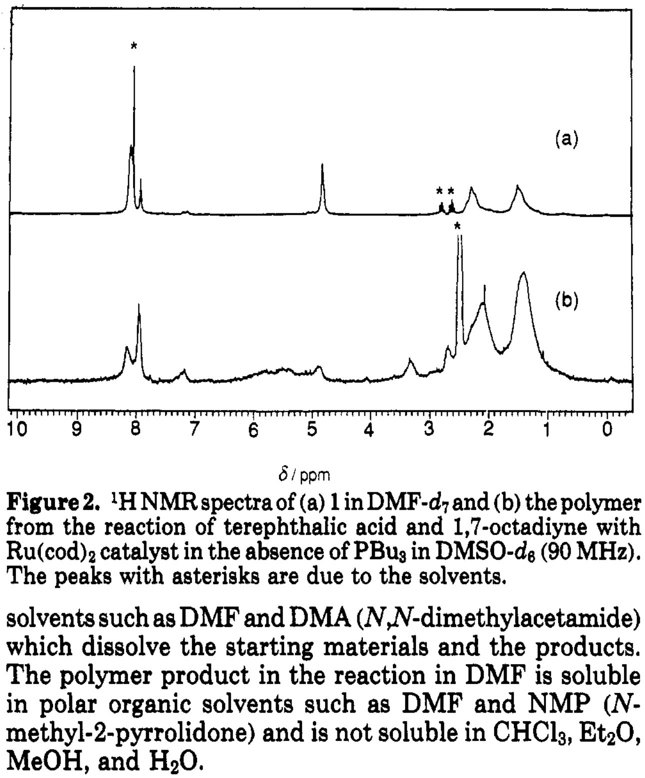


Figure 2. ^1H NMR spectra of (a) 1 in DMF-d_7 and (b) the polymer from the reaction of terephthalic acid and 1,7-octadiyne with $Ru(cod)_2$ catalyst in the absence of PBu_3 in DMSO-d_6 (90 MHz). The peaks with asterisks are due to the solvents.

solvents such as DMF and DMA (*N,N*-dimethylacetamide) which dissolve the starting materials and the products. The polymer product in the reaction in DMF is soluble in polar organic solvents such as DMF and NMP (*N*-methyl-2-pyrrolidone) and is not soluble in $CHCl_3$, Et_2O, MeOH, and H_2O.

The IR and NMR spectra of 1 agree with the above structure as described below. Figure 1 shows the IR spectrum which gives ν(C=O) and ν(C=C) bands of the vinylidene ester group at 1740 and 1660 cm^{-1}, respectively. Figure 2a shows the ^1H NMR spectrum of 1 in DMF-d_7 giving signals due to the $-(CH_2)_4-$ hydrogens at 1.5 and 2.3 ppm and those of the aryl hydrogens at 7.9–8.2 ppm, respectively. The signal of the olefin hydrogens appears at 4.9 ppm as a slightly broadened singlet whose peak pattern agrees with the vinylidene structure rather than vinylene structure which would show the signal of the olefin hydrogens as two doublets with the *J*(HH) value larger than 10 Hz. A model compound, $PhCOO-C(=CH_2)-(CH_2)_4-C(=CH_2)OCOPh$, which is prepared from 1,7-octadiyne and 2 equiv of benzoic acid under similar conditions, also shows the ^1H NMR signal due to olefin hydrogens as a singlet at 4.9 ppm. Figure 3 shows the $^{13}C\{^1H\}$ NMR spectrum of 1, giving C_6H_4 and CH_2 carbon signals at 135.3 and 129.8 ppm and 33.2 and 26.0 ppm, respectively. The signals of the carbonyl carbon and that of quaternary olefin carbon are observed at 167.2 and 157.1 ppm, respectively. The signal due to the methylidene carbon ($=CH_2$) appears at 102.3 ppm, and the ^1H gated decoupled ^{13}C NMR spectrum shows the signal as a triplet with a ^1J(CH) value of 160 Hz. The specific viscosity, $[\eta]_{sp}$, of polymer 1 is obtained as 0.11 dL g^{-1} in the DMF solutions at 30 °C. GPC measurement shows the molecular weights $M_n = 6.6 \times 10^3$ and $M_w = 1.1 \times 10^4$, respectively.

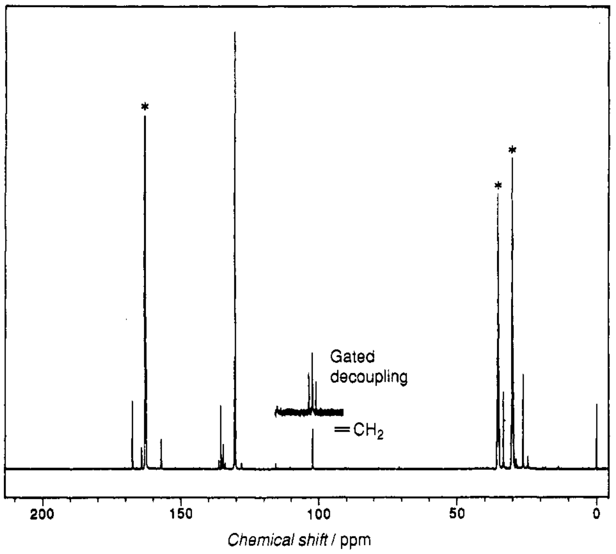
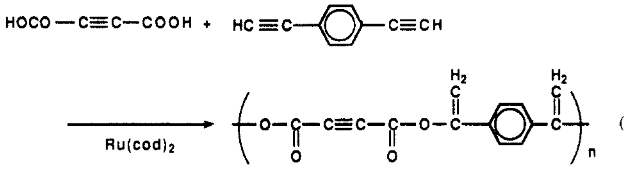


Figure 3. $^{13}C\{^1H\}$ NMR spectrum of 1 at 125 MHz in DMF-d_7. The peaks with asterisks are those of the solvent. The spectrum obtained under ^1H gated decoupling conditions is also shown for the signal at 102.3 ppm.

A similar reaction of terephthalic acid with 1,7-octadiyne by $Ru(cod)_2$ catalyst in the absence of PBu_3 also gives a polymer product as a brown solid which shows IR peaks at 1660 cm^{-1} due to the ν(C=C) vibration, indicating formation of a poly(enol ester) through polyaddition of the dicarboxylic acid to the diyne. M_n and M_w are 1.2×10^4 and 1.7×10^4, respectively, by GPC measurement, and the $[\eta]$ value is 0.11 dL g^{-1}. However, the ^1H NMR spectrum in DMSO-d_6 (Figure 2b), showing the olefin hydrogen signal as broad peaks in the range 6.2–4.9 ppm, indicates a molecular structure containing both vinylidene and vinylene groups. The complicated peak pattern of the olefin hydrogen signal in NMR and the analytical results showing much higher carbon content than that calculated from the polyaddition product seem to be due to an accompanying side reaction involving intermolecular C—C bond formation between two alkynyl groups. The $Ru(cod)_2$ catalyzed addition of carboxylic acid to 1-alkyne in the absence of PBu_3 in THF has been reported to give the enol ester with the vinylene structure,[4] and reaction of 1,7-octadiyne with 2 equiv of benzoic acid catalyzed by $Ru(cod)_2$ in DMF gives a mixture of the enol esters containing *trans*- and *cis*-1,2-vinylene groups and the 1,1-vinylidene group on the basis of the ^1H NMR spectra.

All these results indicate that both $Ru(cod)_2$–PBu_3 catalyzed polyaddition of terephthalic acid with 1,7-octadiyne and the model reaction of benzoic acid with the diyne causes Markovnikov addition to give the product with the vinylidene group, while the reactions without PBu_3 give the mixtures of the product containing several structures of enol ester groups.

Polyaddition of Acetylenedicarboxylic Acid with 1,4-Diethynylbenzene. Acetylenedicarboxylic acid reacts with 1,4-diethynylbenzene in the presence of $Ru(cod)_2$ catalyst to give the polymer $[OCO-C\equiv C-COO-C(=CH_2)-C_6H_4-C(=CH_2)]_n$ (2) whose IR spectrum shows



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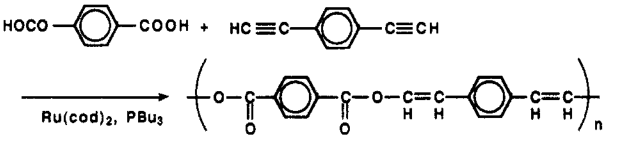
the peaks due to the ν(C=O) and ν(C=C) vibrations at 1720 and 1620 cm^{-1}, respectively. The high solubility of acetylenedicarboxylic acid has enabled the reaction to proceed in THF which cannot be used in reaction 2 due to the low solubility of terephthalic acid. Reaction 3 gives poly(enol ester) **2** with the vinylidene group both in the presence and in the absence of PBu_3. The ^1H NMR spectrum of **2** in DMSO-d_6 shows a singlet signal at 4.4 ppm due to the vinylidene group. The signal due to hydrogens of the vinylene group that would show the peaks at lower magnetic field positions with large HH coupling constants is not observed. Polymer **2**, isolated in 55% yield from the reaction mixture by addition of H_2O, shows a multimodal GPC curve corresponding to the molecular weights M_n = (3.3–7.2) × 10^3 and M_w = (3.3–9.0) × 10^3 (vs polystyrene). Treatment of the reaction mixture with Et_2O gives **2** with a higher molecular weight ($M_n = 1.2 \times 10^4$ and $M_w = 1.7 \times 10^4$) although the yield is much lower (9%). GC and GPC analyses of the resulting solution after reprecipitation of the polymer show the presence of unreacted 1,4-diethynylbenzene and the product with a lower molecular weight (M_n = ca. 1.2×10^3).

Polyaddition of Terephthalic Acid with 1,4-Diethynylbenzene. Reaction of terephthalic acid with 1,4-diethynylbenzene in the presence of $Ru(cod)_2$ catalyst gives poly(enol ester) $[OCO—C_6H_4—COO—CH=CH—C_6H_4—CH=CH]_n$ (**3**) in 66% yield. The polymer is



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sparingly soluble in polar organic solvents such as DMF and DMSO, and practically insoluble in less polar solvents such as $CHCl_3$, acetone, and toluene. The DMF soluble part of the polymer (about 10% of the obtained **3**) has M_n and M_w values of 1.5×10^3 and 4.7×10^3, respectively, as determined by GPC measurement.

The IR spectrum of **3** shows the peaks due to ν(C=O) and ν(C=C) vibrations at 1730 and 1650 cm^{-1}, respectively. The ^1H NMR spectrum of the soluble part of **3** in DMSO-d_6 shows the signals due to the olefin hydrogens at 6.1 and 6.8 ppm as two doublets with J(HH) = 12 Hz. The peak positions and the large coupling constant are quite different from those of polymers **1** and **2** and indicate the molecular structure containing the *cis*-vinylene enol ester group.[8]

The $Ru(cod)_2$ catalyzed addition of carboxylic acids to phenylacetylene has not been reported. The reaction of benzoic acid with phenylacetylene in DMF using the $Ru(cod)_2$–PBu_3 catalyst gives a mixed product, whose ^1H NMR spectrum shows two sets of two doublets due to the olefin hydrogens at 7.2–5.8 ppm (J(HH) = 16 and 12 Hz), revealing that the product is a mixture of *trans*- and *cis*-β-styryl benzoate in a 58:42 ratio. Formation of a mixture of cis and trans products in the model reaction despite selective formation of the cis poly(enol ester) in the above polyaddition is probably due to isomerization of the cis product in the model reaction to the trans under the conditions.

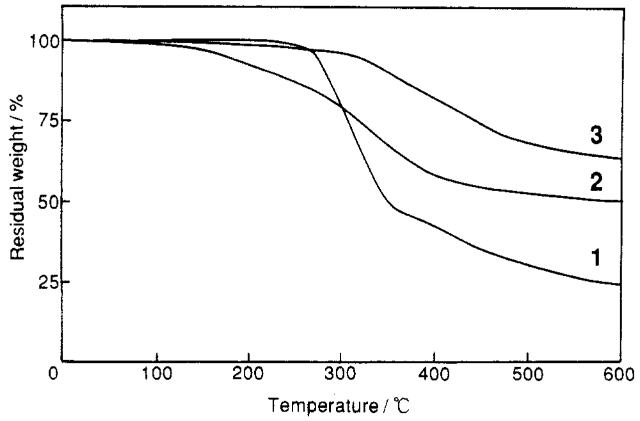


Figure 4. TG curves of **1**–**3** under N_2 with a temperature raising rate of 10 °C min^{-1}.

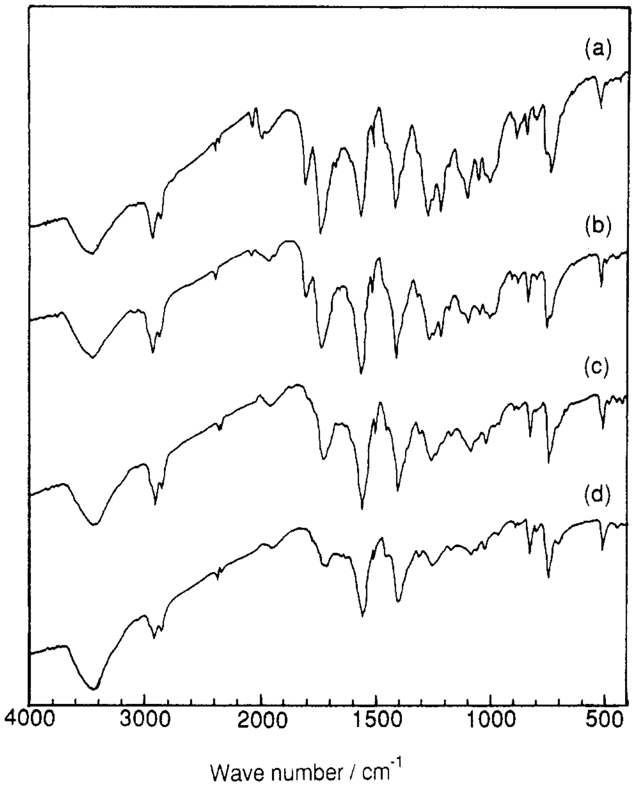


Figure 5. Change of the IR spectrum of **1** during TG measurement under N_2 with the temperature raising rate of 10 °C min^{-1}. The spectra are at (a) 275 °C, (b) 300 °C, (c) 325 °C, and (d) 350 °C, respectively.

Although the detailed structure of the DMSO insoluble part of **3** is not analyzed by NMR spectroscopy due to the poor solubility, it probably has the structure with the vinylene group, similar to that of the DMSO soluble part, because both the DMSO soluble part and insoluble parts of **1** show IR spectra quite similar to each other.

Thermal Properties of the Polymers. Polymers **1**–**3** undergo thermal decomposition without melting. Figure 4 shows the TG curves of the polymers. Polymer **1** shows a sharp weight loss in the range 270–340 °C although **2** and **3** show gradual weight decrease in a wider temperature ranges. The poly(enol ester) prepared from terephthalic acid and 1,7-octadiyne using $Ru(cod)_2$ catalyst in the absence of PBu_3 shows a multistep weight decrease in the range 100–500 °C, indicating the presence of several molecular structures in the polymer, as was also revealed by the NMR spectra. Figure 5 shows a change of the IR spectra of **1** during the TG measurement. A significant decrease of the ν(C=O) peak is observed in the range 275–350 °C, during which the sharp weight loss of the polymer occurs. Decomposition of the enol ester moiety in the molecule seems to occur at the initial stage of pyrolysis of the polymer.

Polymerization Mechanism. The Ru(cod)$_2$ catalyzed polyaddition of dicarboxylic acids with diynes in the present study gives Markovnikov or anti-Markovnikov addition products depending on the kind of substrate. The selectivity of the reaction of terephthalic acid with 1,7-octadiyne is influenced by the presence or absence of PBu$_3$, similarly to the related reaction of benzoic acid with 1-alkynes giving vinyl esters. Two reaction pathways have been proposed for Markovnikov and anti-Markovnikov addition, respectively. Results of the kinetic measurement and of the deuterium isotope labeling experiments of the Ru(cod)$_2$–PBu$_3$ catalyzed reaction to give Markovnikov addition products agree with the pathway involving nucleophilic attack of the carboxylate group on a coordinated alkyne carbon bonded to the ruthenium center to give the hydride(vinyl)ruthenium intermediate that undergoes ensuing reductive elimination of the vinyl ester having the vinylidene group.[4,9] The rhodium complex with the 1-alkyne ligand reacts with carboxylic acid to give the enol ester also through Markovnikov addition.[10] On the other hand, reaction of several (carboxylato)ruthenium complexes with 1-alkynes leads to apparent *anti*-Markovnikov addition of the carboxylate to the alkyne.[11-13] These results suggest that the vinylidene and vinylene isomers of the enol ester in the Ru complex catalyzed reactions are formed through different reaction pathways and that addition of PBu$_3$ to the reaction mixture causes an increase in the relative stability of the alkyne-coordinated intermediate, as compared to another possible intermediate (carboxylato)ruthenium complex, to enhance the former reaction pathway. On the basis of the above observations a probable mechanism for the present polyaddition is summarized in Scheme 2. The poly(enol ester) with the vinylidene structure seems to be formed by repetition of addition of a COOH group to the coordinated alkyne to give the vinylruthenium species that will undergo facile substitution by 1-alkyne, similarly to path i in the above scheme.

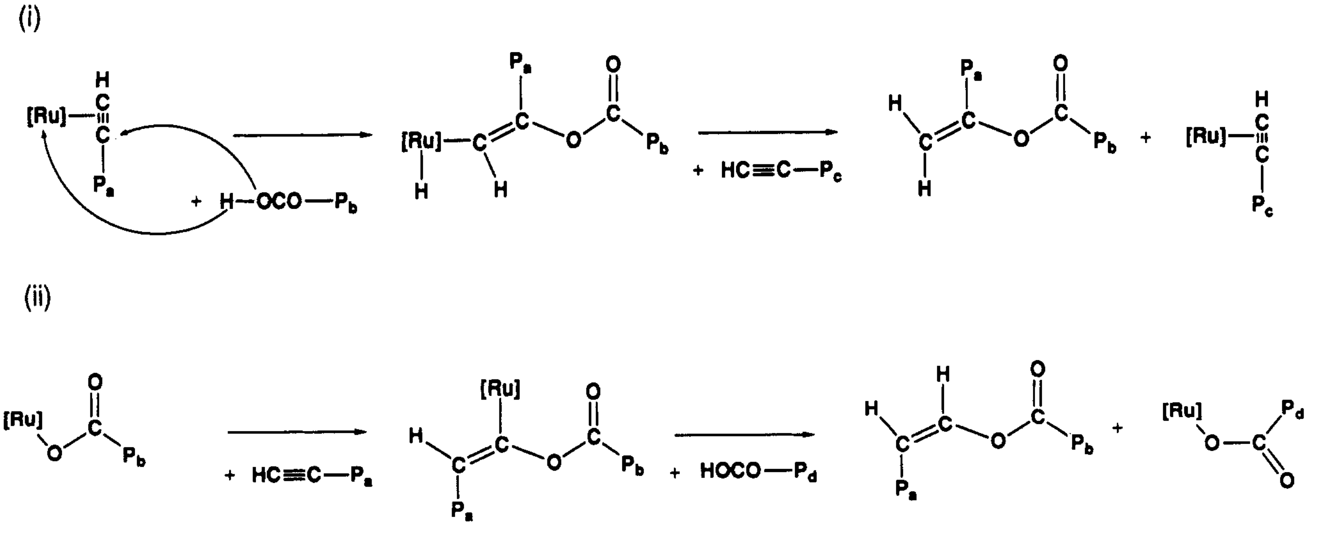
Scope and Limitation of the Polymer Synthesis. The Ru complex catalyzed addition of carboxylic acid to alkyne has been developed to synthesize several poly(enol ester)s. The polymers with the vinylidene or vinylene group are obtained depending on the substrates and the reaction conditions. The analytical results and the NMR spectra indicate 1:1 polyaddition in most of the reactions in the present study. Although yields and molecular weights of the products are not high, a similar type of metal complex catalyzed polyaddition of other substrates or that by another catalyst would give novel poly(enol ester)s with sufficiently high molecular weights and with new chemical or physical properties.

Experimental Section

General Materials and Measurement. All the manipulations of the ruthenium complexes and polymerization were carried out under nitrogen or argon using standard Schlenk techniques. The solvents were dried by the usual method, distilled, and stored under nitrogen. Ru(cod)$_2$, RuCl$_2$(*p*-cymene)(PPh$_3$), and 1,4-diethynylbenzene were prepared according to the literature.[14-16] Other organic chemicals were purchased and used as received. IR spectra were recorded on a JASCO-IR810 spectrophotometer. NMR spectra (^{1}H and ^{13}C) were recorded on JEOL EX-90 and GX-500 spectrometers. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. GC was measured on a Shimadzu GC-6A using Silicon OV-1 (2%). GPC analyses were carried out by a Toso HLC-8020 using a DMF solution of LiBr (0.01 M) as the eluent and polystyrene as the standard.

Polyaddition of Terephthalic Acid with 1,7-Octadiyne by the Ru(cod)$_2$-PBu$_3$ Catalyst. A mixture of Ru(cod)$_2$ (83 mg, 0.26 mmol), PBu$_3$ (110 mg, 0.54 mmol), and maleic anhydride (51 mg, 0.52 mmol) was dissolved in DMF (15 mL). After the solution was stirred at room temperature for 10 min, 1,7-octadiyne (560 mg, 5.3 mmol) and terephthalic acid (880 mg, 5.3 mmol) were added. The reaction mixture was stirred at room temperature until complete dissolution of the monomers and was heated at 100 °C for 15 h with stirring. The reaction products were poured into MeOH (ca. 200 mL) to cause precipitation of a brown solid, which was filtered, washed with 0.5 N NaOH(aq) and then with hexane and acetone, and dried in vacuo (400 mg, 28%). ^{1}H NMR (90 MHz in DMF-d_7): δ 1.5 and 2.3 (m, CH$_2$), 4.9 (s, =CH$_2$), 8.1 (s, C$_6$H$_4$). Anal. Calcd for C$_{16}$H$_{16}$O$_4$: C, 70.6; H, 5.9. Found: C, 67.5; H, 5.6.

Scheme 2. Possible Pathways for the Formation of Poly(enol ester)s with (i) a Vinylidene Structure and with (ii) a Vinylene Structure Based on the Results of Mechanistic Studies of the Reaction of Carboxylic Acid with 1-Alkyne



P$_a$, P$_c$ = polymer chain or Y-C≡CH (in monomer HC≡C-Y-C≡CH)

P$_b$, P$_d$ = polymer chain or X–COOH (in monomer, HOCO–X–COOH)

Polyaddition of the monomers by Ru(cod)$_2$ catalyst in the absence of PBu$_3$ was carried out analogously. The polymer product was obtained in a 37% yield. ^{1}H NMR (90 MHz in DMSO-d_6): δ 1.2–2.5 (m, CH$_2$), 4.9 (s, $=$CH$_2$), 5.2–6.0 (m, –CH$=$CH–), 8.1 (m, C_6H_4). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.1; H, 5.9. Found: C, 77.4; H, 8.2.

Reaction of Benzoic Acid with 1,7-Octadiyne Catalyzed by the Ru(cod)$_2$–PBu$_3$ Catalyst. A mixture of Ru(cod)$_2$ (35 mg. 0.11 mmol), PBu$_3$ (44 mg, 0.22 mmol), and maleic anhydride (22 mg, 0.22 mmol) was dissolved in DMF (10 mL). After the solution was stirred at room temperature for 10 min, 1,7-octadiyne (240 mg, 2.3 mmol) and benzoic acid (540 mg, 4.4 mmol) were added. The reaction mixture was heated at 100 °C for 8.5 h with stirring. After evaporation of the solvent, the oily product was washed with 1N NaOH(aq) and extracted with Et$_2$O. Chromatography on an alumina column (eluent CHCl$_3$) gives PhCOO—C(=CH$_2$)—(CH$_2$)$_4$—C(=CH$_2$)—OCOPh as the brown liquid (470 mg, 58%). ^{1}H NMR (90 MHz, in CDCl$_3$): δ 1.2–2.5 (m, 8H, CH$_2$), 4.9 (s, 2H, =CH$_2$), 7.3–8.3 (m, 10H, C_6H_5).

Reaction in the absence of PBu$_3$ gave the product as a brown liquid (52%) which was composed of several structural isomers. ^{1}H NMR (90 MHz, in CDCl$_3$: δ 1.2–2.5 (m, 8H, CH$_2$) 4.9 (s), 5.0–5.7 (dd, J(HH) = 15 Hz), 7.3–8.3 (m, 10H, C_6H_5).

Polyaddition of Acetylenedicarboxylic Acid with 1,4-Diethynylbenzene by the Ru(cod)$_2$ Catalyst. To a THF (10 mL) solution of Ru(cod)$_2$ (26 mg, 0.08 mmol) were added acetylenedicarboxylic acid (450 mg, 4.0 mmol) and 1,4-diethynylbenzene (500 mg, 4.0 mmol) in that order. The mixture was heated under reflux for 14 h. The reaction products were poured into H$_2$O (ca. 200 mL) to cause precipitation of [OCOC≡CCOO—C(=CH$_2$)—C_6H_4—C(=CH$_2$)]$_n$ (**2**) as a brown solid, which was filtered out, washed with Et$_2$O and hexane, and dried in vacuo (520 mg, 55%). ^{1}H NMR (90 MHz in DMSO-d_6): δ 4.4 (s, =CH$_2$), 7.1 (s, C_6H_4). Anal. Calcd for $C_{12}H_8O_4$: C, 66.7; H, 3.7. Found: C, 64.6; H, 4.9.

Addition of Et$_2$O (200 mL) to the reaction gives **2** in 9% yield.

Polyaddition of Terephthalic Acid with 1,4-Diethynylbenzene. A mixture of Ru(cod)$_2$ (65 mg, 0.20 mmol), PBu$_3$ (100 mg, 0.51 mmol), and maleic anhydride (40 mg, 0.41 mmol) was dissolved in DMF (10 mL). After the solution was stirred at room temperature for 10 min, 1,4-diethynylbenzene (200 mg, 1.6 mmol) and terephthalic acid (270 mg, 1.6 mmol) were added. The resulting mixture was stirred at room temperature until complete dissolution of the monomers and was heated at 100 °C for 15 h with stirring. The reaction products were poured into MeOH (ca. 400 mL) to cause precipitation of [OCO—C_6H_4—COO—CH=CH—C_6H_4—CH=CH]$_n$ (**3**) as a brown solid, which was filtered out and dried in vacuo (310 mg, 66%). ^{1}H NMR of the DMF soluble part (ca. 10% of the product) (90 MHz in DMSO-d_6): δ 6.1 and 6.8 (d, -HC=CH- (cis), J = 12 Hz), 7.1–7.9 (m, C_6H_4). Anal. Calcd for $C_{18}H_{12}O_4$: C, 76.1; H, 4.8. Found: C, 76.2; H, 4.1.

Reaction of Benzoic Acid with Phenylacetylene Catalyzed by Ru(cod)$_2$–PBu$_3$. A mixture of Ru(cod)$_2$ (29 mg, 0.092 mmol), PBu$_3$ (36 mg, 0.18 mmol), and maleic anhydride (17 mg, 0.18 mmol) was dissolved in toluene (5 mL). After the solution was stirred at room temperature for 10 min, phenylacetylene (940 mg, 9.2 mmol) and benzoic acid (1.2 g, 10 mmol) were added. The resulting red solution was heated at 80 °C for 14 h with stirring. After evaporation of the solvent the resulting solid product was purified by column chromatography (alumina, CHCl$_3$) to give a mixture of *trans*- and *cis*-β-styryl benzoate as a brown solid (1.5 g, 73%). ^{1}H NMR (90 MHz in DMSO-d_6): δ 5.9 and 6.7 (d, HC=CH (cis), J = 12 Hz), 6.4 and 7.0 (d, HC=CH (trans), J = 16 Hz), 7.1–8.0 (m, C_6H_4).

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