5168 *Macromolecules* **1999,** *32,* 5168−5170

Asymmetric Terpolymerization of Propene, Vinylarene, and Carbon Monoxide

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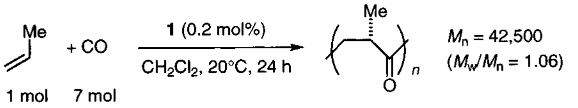
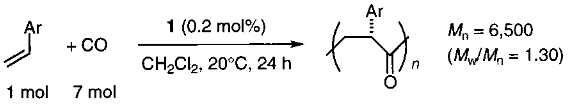
Received February 24, 1999
Revised Manuscript Received April 15, 1999

Alternating copolymerization of olefins with CO is a recent topic from the viewpoints of homogeneous catalysis, organometallic chemistry, and polymer synthesis.[1] Palladium(II) complexes are mostly used and bidentate bisphosphines[2] and related bidentate phosphorus ligands[3] are known to be effective for the copolymerization of ethene, propene, or higher 1-alkenes with CO, on one hand. On the other hand, nitrogen-based ligands, such as diimine (or bipyridyl),[4] bisoxazoline,[5] and phosphine−imine,[6] have been utilized for the copolymerization of vinylarenes with CO. Asymmetric synthesis polymerization[7] is an attractive subject in the case of α-olefins, and successful examples were reported for both propene−CO copolymerization with chiral phosphorus ligands[2a,b,3] and vinylarene−CO copolymerization with chiral nitrogen ligands.[4a,d,5,6] In contrast to the intensive efforts devoted to the copolymer synthesis, however, much less has been reported on terpolymer synthesis. A few reports appeared on ethene−vinylarene−CO terpolymerization with chiral[4a,6] and achiral[4b,c,e] nitrogen ligands and only one example is known to us for propene−vinylarene−CO terpolymerization using an achiral ligand, 1,10-phenanthroline.[4b,c] We recently disclosed that the Pd(II) complex of a chiral phosphine−phosphite, $[Pd(CH_3)(CH_3CN)\{(R,S)\text{-BINAPHOS}\}]\cdot[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ (**1**), catalyzes asymmetric copolymerization of propene with CO in a highly enantioselective fashion (eq 1).[3] The system was also applicable to the copolymerization of 4-*tert*-butylstyrene−CO (eq 2).[3b] As a phosphorus-based compound, this is the first example of an effective ligand for vinylarene−CO copolymerization. With this unique catalyst in hand, here we report the asymmetric terpolymerization of propene, 4-*tert*-butylstyrene, and CO.

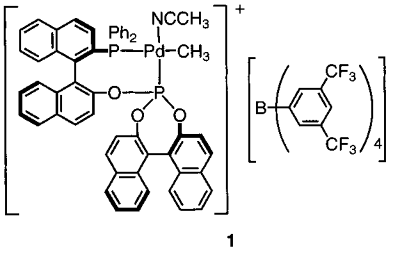


(1)



(2)

Ar = 4-*tert*-Bu-C$_6$H$_4$



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A mixture of propene and 4-*tert*-butylstyrene was treated with an excess amount of CO in the presence of **1** for 24 h at 20 °C, affording a polymer which contained unit (propene-*alt*-CO), namely, unit A, and unit (4-*tert*-butylstyrene-*alt*-CO), namely, unit B. The ratio of unit A/unit B in the product (=*a*/*b*) was determined by ^{1}H NMR.[8] Thin-layer chromatography analysis of the polymer manifested the coexistence of both units A and B in a single molecule.[9] With change in the initial partial pressure of propene (Table 1, runs 1−3) or initial concentration of 4-*tert*-butylstyrene (runs 1 and 4−5), the *a*/*b* ratio could be made to vary. The higher propene/4-*tert*-butylstyrene ratio increased the *a*/*b* ratio and the molecular weight of the product while a slight decrease in M_w/M_n was observed. Employing the monomer ratio of run 1, the reaction was stopped after 3, 6, and 12 h and the produced polymers were analyzed (runs 6−8). With prolonging the reaction time, the total yield of the terpolymer successively increased, but the molecular weight stays around M_n = 8000−10000. The above observations can be interpreted as follows: (1) The polymerization process is not in a living mode for the present terpolymerization. This is in sharp contrast to the living nature of the propene−CO alternating copolymerization with the same catalyst system as was revealed in our previous study.[3b] (2) The chain termination is accelerated at the higher initial concentration of 4-*tert*-butylstyrene relative to propene. This caused the decrease of the molecular weight and increased M_w/M_n. The β-hydride elimination from the alkyl−Pd species seems most probable for the current chain transfer. Short oligomer formation was reported from styrene and CO due to the easy β-hydride elimination when bisphosphine−Pd complexes were used as catalysts.[10,11]

The ^{13}C NMR of the terpolymer of run 1 of Table 1 is shown in Figure 1(i). As references, the charts of copolymers isotactic poly(propene-*alt*-CO) (from eq 1) and isotactic poly(4-*tert*-butylstyrene-*alt*-CO) (from eq 2) are compared as Figure, parts 1 (ii) and (iii), respectively. Chart (i) is essentially superimposable to the sum of (ii) and (iii). The incorporated olefin ratio *a*/*b* is reflected in three such pairs of peaks, namely, δ 211.2−212.6 ($-CH_2-CHMe-C(=O)-$) and 207.0−208.2 ($-CH_2-CHAr-C(=O)-$); δ 44.7 ($-CH_2-CHMe-C(=O)-$) and 45.0 ($-CH_2-CHAr-C(=O)-$); and δ 40.0 ($-CH_2-CHMe-C(=O)-$) and 51.9 ($-CH_2-CHAr-C(=O)-$).[8] The absence of any other peak suggests the completely alternating copolymerization between the olefin and CO. For the vinylarene−CO moiety, $-CH_2-CHAr-C(=O)-$, a head-to-tail and isotactic structure is more probable because of the following two facts: (1) The carbon peaks of the terpolymer at δ 45.0 and 51.9 are closer to the peaks of an isotactic structure at δ 45.6 and 51.7 (shown in Figure 1(iii)) than to those of a syndiotactic structure at δ 43.0 and 52.7.[5a] (2) The aromatic proton peaks of the terpolymer were observed at δ 6.85−7.15 and 7.20−7.38, matching the δ 6.84 and 7.17 of the isotactic structure rather than δ 6.57 and 6.99 of the syndiotactic strucuture.[5a,8] In regard to the propene−CO moiety, it is clear that the moiety has a head-to-tail structure rather than either a head-to-head or a tail-to-tail structure. The carbonyl carbon peak was

10.1021/ma9902807 CCC: $18.00

Table 1. Asymmetric Terpolymerization of Propene, 4-^{t}Butylstyrene, and Carbon Monoxide Catalyzed by 1[a]

run	propene (atm)	4-^{t}bu−styrene (*M*)	time (h)	product (mg)	*a*/*b*	yield (%) from		M_n	M_w/M_n	$[\alpha]_D$[b]	$[\Phi]_{Dmeasured}$[c]	$[\Phi]_{Dcalcd}$[c]
						propene	4-^{t}bu−styrene					
1	1	1.02	24	112.1	1.85	31.4	5.6	8100	1.5	−220	−249	−204
2	3	1.02	24	172.1	11.0	31.0	3.1	28000	1.2	−125	−115	−86
3	6	1.02	24	227.9	23.7	23.3	2.0	30200	1.3	−98	−81	−63
4	1	0.51	24	89.5	3.38	34.2	6.7	14800	1.3	−191	−198	−148
5	1	2.04	24	102.6	0.79	16.0	3.4	8500	1.4	−206	−283	−299
6	1	1.02	3	28.5	1.67	7.5	1.5	8400	1.2	−200	−239	−215
7	1	1.02	6	47.7	1.47	11.6	2.6	9400	1.3	−201	−246	−229
8	1	1.02	12	61.4	1.50	15.1	3.4	10500	1.3	−220	−269	−227

[a] After treatment of a solution of **1** (22.4 mg, 0.0125 mmol) in CH_2Cl_2 (5.0 mL) with CO (1 atm), 4-*tert*-butylstyrene (6.24 mmol, for runs 1−3 and 6−8) was added and the mixture was then stirred in a 50 mL autoclave under a mixture of propene and CO (20 atm) for 24 h at 20 °C. Precipitation from CH_3OH (100 mL) gave poly{(propene; 4-*tert*-butylstyrene)-*alt*-CO}. [b] $c = 0.49{-}0.57$ (w/v %) in $CHCl_3$. Temperature was in the range of 25.6−26.8 °C. [c] See text for the definitions of $[\Phi]_{Dmeasured}$ and $[\Phi]_{Dcalcd}$.

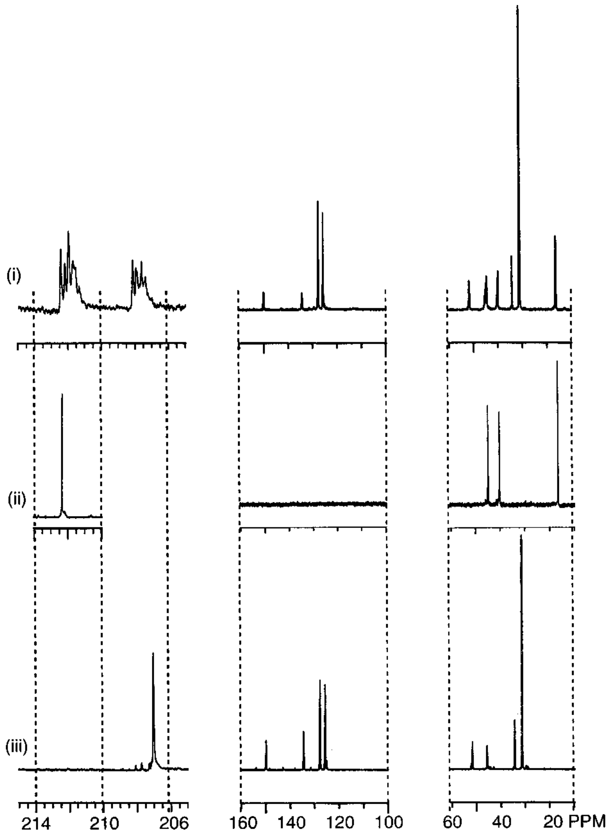
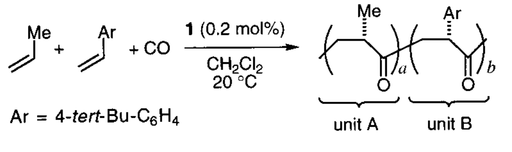


Figure 1. ^{13}C NMR ($CDCl_3$) of (i) poly{(propene; 4-*tert*-butylstyrene)-*alt*-CO}, (ii) poly(propene-*alt*-CO), and (iii) poly(4-*tert*-butylstyrene-*alt*-CO).

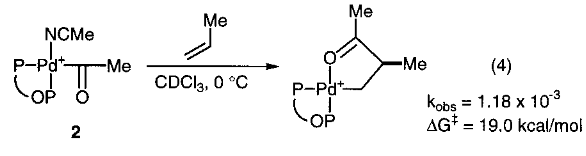
observed at δ 211.2−212.6, in the region of head-to-tail δ 211−213, but not in either head-to-head δ 214−216, or tail-to-tail δ 207−208.[2c] Considering that almost completely isotactic poly(propene-*alt*-CO) was obtained by the catalyst control of **1** (eq 1 and Figure 1(ii)),[3a,b] the structure drawn in eq 3 is proposed for the terpolymer. As shown, both propene and the vinylarene are incorportated in a head-to-tail and isotactic manner.[12] Furthermore, some of the peaks of Figure 1(i) split into several peaks because of the difference in the neighboring groups. This may be attributed to the rather random incorporation of two kinds of olefins than to any sort of regularity.



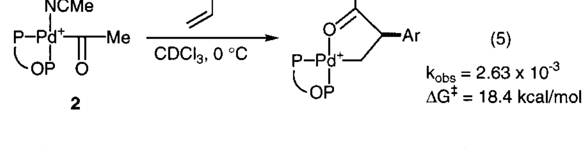
(3)

The optical purity of the chirotopic carbons was estimated by the optical rotation. The $[\Phi]_D$ values of poly(propene-*alt*-CO) and poly(4-*tert*-butylstyrene-*alt*-CO) in $CHCl_3$ were −44.0 and −501.3, respectively, when the polymers were prepared under the same conditions.[3b] In solution, the optical rotation of poly(propene-*alt*-CO) is reported to arise only from the chirotopic carbons of the main chain, but not from any higher-order polymer structures such as a stable helical conformation.[2a,4a,13] Here, if we assume that this is also the case for the present terpolymer, its molar optical rotation $[\Phi]_D$ can be estimated by calculation as $[\Phi]_{Dcalcd.} = \{(-44.0)a + (-501.3)b\}/(a + b)$. Experimentally, the optical rotation value $[\alpha]_D$ was measured for the terpolymers and the values were converted into molar optical rotation as $[\Phi]_{Dmeasured} = [\alpha]_D \times M/100$, where M is the average molecular weight per unit. Using the unit molecular weight for $[CH_2{-}CHMe{-}C({=}O)]$ (70.1) and $[CH_2{-}CH(C_6H_4{-}t\text{-}Bu){-}C({=}O)]$ (188.3), it is expressed as $M = \{(70.1)a + (188.3)b\}/(a + b)$. The similarity between $[\Phi]_{Dcalcd.}$ and $[\Phi]_{Dmeasured.}$ supports the validity of the above assumption. In addition, it is suggested that the enantioface of each olefin was selected by the catalyst at its incorporation step, regardless of the kind of the preceding olefins. In other words, the enantioselectivity for the olefin was as high as that observed in the copolymerization of propene−CO and of 4-*tert*-butylstyrene−CO.

The reaction rate of olefin insertion to an acylpalladium species was measured for each olefin. In our previous study,[3b] a $CDCl_3$ solution of $[Pd(C({=}O)CH_3)(CH_3CN)\{(R,S)\text{-BINAPHOS}\}]\cdot[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ (**2**) was treated with a large excess (30 equiv) of propene at 0 °C to measure the rate constant k_{obs} and the activation energy $\Delta G^‡$ for the reaction of 1.18×10^{-3} s^{-1} and 19.0 kcal/mol, respectively (eq 4). Similarly, the decay of **2** was measured in the presence of 4-*tert*-butylstyrene[14] and here we obtained the values of 2.63×10^{-3} s^{-1} and 18.4 kcal/mol, respectively (eq 5).[12] Thus, the insertion rate for 4-*tert*-butylstyrene into **2** is similar



(4)



(5)

to, or even slightly faster than, that for propene. This result contradicts the preferable incorporation of propene observed in Table 1. Similar conflict was reported by Consiglio for the terpolymerization of ethene, styrene, and carbon monoxide.[6] They also found that the ethene content in the random copolymer is higher than that of styrene, although styrene–CO alternating copolymerization proceeds much faster than that of ethene–CO with their Pd(II)–phosphine–imine catalyst. The reason for this fact is not clear yet at this moment.

In conclusion, we have prepared the terpolymer of propene, 4-*tert*-butylstyrene, and carbon monoxide in an asymmetric manner for the first time. During the current terpolymerization, the olefins were incorporated in a head-to-tail and isotactic fashion. The enantioface of each olefin was selected by the catalyst, with similar completeness to that observed in the copolymerization of propene–CO and of 4-*tert*-butylstyrene–CO. The preferable incorporation of propene was observed compared to 4-*tert*-butylstyrene, although the kinetic studies suggested that 4-*tert*-butylstyrene was more reactive toward the insertion to acylpalladium **2**.

Acknowledgment. This work was supported by NEDO for the project on Technology for Novel High-Functional Materials in Industrial Science and Technology Frontier Program, AIST.

Supporting Information Available: Experimentals for the synthesis of polymers and for the kinetic studies are described. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The original charts and detailed peak assignments are included in the Supporting Information.

(9) The R_f values for copolymers poly(4-*tert*-butylstyrene-*alt*-CO) and poly(propene-*alt*-CO) and the polymer obtained here were 0.85, 0.00, and 0.00, respectively (Merk, Silica gel 60 F_{254}, $CHCl_3$). Because the spot for a pure poly(4-*tert*-butylstyrene-*alt*-CO) was not detectable in the current product, the coexistence of both units A and B in one molecule has been disclosed.

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(11) The polymer prepared in run1 of Table 1 showed a doublet at δ 6.63 (J = 16.0 Hz) due to (E)-ArCH=CH–C(=O)– in ^{1}H NMR.[8] On the basis of the integration, the molecular weight of 10800 can be calculated. Thus, the β-hydride elimination from Pd–CHAr–CH_2–C(=O)– is suggested to be the most probable step for the chain termination. This species results from the 2,1-insertion of the vinylarene.

(12) Although the regioselectivity for the vinylarene insertion is not clear at this moment, 1,2-insertion is tentatively drawn in eqs 3 and 5. The head-to-tail structure matches the ^{13}C NMR charts. A possible 1,2-insertion of styrene was reported by Consiglio very recently. See ref 6b.

(13) In a solid amorphous state, the existence of a stable secondary structure is suggested for poly(4-*tert*-butylstyrene-*alt*-CO) but not in a solution. Muellers, B. T.; Green, M. M.; Brookhart, M. *Polym. Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 709.

(14) In eq 5, only the decay of **2** was measured. Because of the β-hydride elimination and reinsertion,[15] several species were detected as products by ^{31}P NMR.

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