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Electroorganic Reactions on Organic Electrodes. 6. Electrochemical Asymmetric Oxidation of Unsymmetric Sulfides to the Corresponding Chiral Sulfoxides on Poly(amino acid)-Coated Electrodes†

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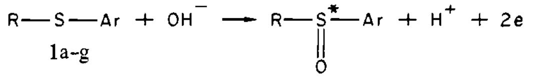
Abstract: Alkyl aryl sulfides (**1a–g**) were electrochemically oxidized to the corresponding chiral sulfoxides (**2a–g**) (eq 1) by using poly(amino acid)-coated electrodes. The highest optical yield was 93%, which was obtained in the oxidation of *tert*-butyl phenyl sulfide (**1e**) to *tert*-butyl phenyl sulfoxide (**2e**) on a platinum electrode coated doubly with polypyrrole and poly(L-valine).

Although a variety of methods for preparing optically active sulfoxides had been reported, very few methods had afforded such sulfoxides with high optical purities. Mislow et al.[1] obtained 47–85% of optical yields in the transformation of chiral toluenesulfinate esters to the corresponding chiral alkyl tolyl sulfoxides by using alkylmagnesium halides. The starting sulfinate esters must be highly optically pure to obtain the highly optically pure sulfoxides by this method, since maximum optical purities of the sulfoxides cannot be higher than values of the optical yields in the asymmetric transformation. Optical resolution is one of common methods to obtain optically active compounds, but it may be generally unfavorable to apply this method to simple sulfoxides having no functional groups which can react with resolving reagents to give the corresponding diastereomeric mixtures; Mikolajczyk and Drabowicz[2] optically resolved such simple sulfoxides by using β-cyclodextrin as a resolving reagent, but their optical purities were as low as 1.1–14.5%. Pirkle and Rinaldi[3] reported an interesting method for the asymmetric transformation of racemic sulfoxides in chiral media. They found that the enantiomeric equilibration of alkyl aryl sulfoxides in chiral cholesteric liquid crystals afforded 0–9.2% of enantiomeric excesses.

The asymmetric oxidation of sulfides should be another important one of methods for preparing optically active sulfoxides. Higuchi et al.[4] oxidized methyl benzyl sulfide with iodine in a chiral buffer solution (pH 6.0) containing *d*-2-methyl-2-phenylsuccinic acid to obtain (*R*)-methyl benzyl sulfoxide in 6.4% of optical yield. Although the asymmetric oxidation of sulfides with chiral oxidizing reagents has been successively investigated, it has not given any satisfactory results: chiral peracids[5-12] and *N*-halides[13] gave 20%[9] and 2.76%[13] of maximum optical yields, respectively. On the other hand, the biochemical oxidation of sulfides with microorganisms, e.g., *Aspergillus niger*, under aerobic conditions resulted in moderate or high optical yields (4–100%) which were greatly affected by substituents of the sulfides.[14-17] Sugimoto et al.[18,19] reported that the oxidation of alkyl aryl sulfides with hydrogen peroxide in the presence of bovine serum albumin afforded the corresponding optically active sulfoxides in 1–81% optical yields which were affected by the substituents.

Electrochemical asymmetric reduction has been successively reported as summarized by Tilborg and Smit[20] and as appeared in later literatures,[21-26] while papers dealing with oxidation have been very rarely published. The first report of the electrochemical asymmetric oxidation was made by Firth et al. They reported low optical yields of 0.3–2.5% in the oxidation of methyl aryl sulfides to the corresponding sulfoxides on electrodes modified chemically with optically active compounds such as phenylalanine ethyl ester[27] and camphoric acid.[28] We also have recently found that cyclohexyl phenyl sulfide (**1f**) can be oxidized to cyclohexyl phenyl sulfoxide (**2f**) in remarkably higher optical yields (28–54%) on poly(L-valine)-coated platinum electrodes.[29]

In this work, the oxidation of a variety of alkyl aryl sulfides (**1a–g**) to the sulfoxides (**2a–g**) (eq 1) was investigated in detail



$$\mathrm{R{-}S{-}Ar} + \mathrm{OH^-} \longrightarrow \mathrm{R{-}\underset{\substack{\| \\ O}}{\overset{*}{S}}{-}Ar} + \mathrm{H^+} + 2e \qquad (1)$$

1a-g

2a-g

a, R = methyl; Ar = phenyl
b, R = isopropyl; Ar = phenyl
c, R = *n*-butyl; Ar = phenyl
d, R = isobutyl; Ar = phenyl
e, R = *tert*-butyl; Ar = phenyl
f, R = cyclohexyl; Ar = phenyl
g, R = cyclohexyl; Ar = *p*-tolyl

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† Stereochemical Studies of the Electrolytic Reactions of Organic Compounds. 25.

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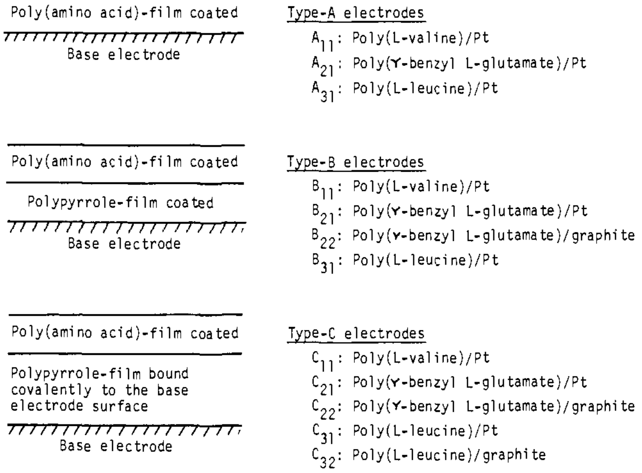

Figure 1. Poly(amino acid)-coated electrodes.

by using various kinds of poly(amino acid)-coated electrodes.

Results and Discussion

Poly(amino acid)-Coated Electrodes. Three types (A, B, and C in Figure 1) of the coated electrodes[30] were prepared and used for the asymmetric oxidation. Type A electrodes were prepared by dipping a base electrode (platinum plate) into poly(amino acid) solutions. To prepare the type B electrodes, the base electrodes (platinum and graphite plates) were first coated with polypyrrole by anodic polymerization and then with poly(amino acid)s in layers by a dipping method similar to above. The type C electrodes were also prepared by double coating with polypyrrole and poly(amino acid)s. Polypyrrole films in this case were covalently bound by $OSi(CH_2)_3N$(pyrrole nucleus) bonding to the base electrode surface. Coating of the polypyrrole films was carried out by a modified method of Simon et al.,[31] who developed the original method for the protection of n-type silicon photoanodes. The base electrodes (platinum and graphite plates) were chemically modified with monomeric pyrrole by the reaction of their surface oxides with *N*-[3-(trimethoxysilyl)propyl]pyrrole and then were anodically treated to polymerize the monomeric pyrrole. The polypyrrole-coated electrodes prepared thus were also coated with poly(amino acid)s by the dipping method.

It seemed difficult to estimate accurately the coating thickness of electrodes doubly coated with polypyrrole and poly(amino acid)s. Amounts of polypyrrole modified chemically and poly(L-valine) coated in 0.5% w/v dip-coating solution were estimated roughly to be 10^{-4} and 10^{-6} g cm^{-2}, respectively, in the case of the C_{11} electrode from weight differences in the electrode before and after coating.

Asymmetric Oxidation on Poly(amino acid)-Coated Electrodes. Electrolyses of sulfides **1a**–**g** were carried out by means of a controlled-potential method in acetonitrile containing tetra-*n*-butylammonium tetrafluoroborate and water as supporting electrolyte and oxygen source, respectively. Electrolytic results are summarized in Table I.

The asymmetric oxidation of methyl phenyl sulfide (**1a**) to the corresponding sulfoxide (**2a**) on several kinds of type A and B electrodes (runs 1–8) gave such low optical yields that it was not worthy asymmetric synthesis. It may be interesting that the increase of water content in the electrolytic solution resulted in the increase of current efficiency for **2a** (run 3).

On the other hand, much higher optical yields were obtained in the oxidation of isopropyl phenyl sulfide (**1b**) (runs 9–13). Especially, a type C electrode, which was constructed by dip-coating a platinum electrode modified chemically with polypyrrole doubly with poly(L-valine), gave a very high optical yield, 73% (run 11). The decrease of concentration of dip-coating solution resulted in the increase of optical yield (77% in run 12).

Optical yields in the oxidation of *n*-butyl phenyl sulfide (**1c**) were as moderate as 7–20% (runs 13–15).

Isobutyl phenyl sulfide (**1d**) (runs 16–19) gave higher and lower optical yields than **1c** and **1b**, respectively. Similarly to the oxidation of **1b**, the decrease of the concentration of the dip-coating solution resulted in the increase of optical yield (run 19).

The asymmetric oxidation was investigated in detail by using *tert*-butyl phenyl sulfide (**1e**) (runs 20–38). Among the type A electrodes (runs 21–23), A_{11} electrode coated with poly(L-valine) gave the highest optical yield (run 21) under the same conditions while A_{31} electrode coated with poly(L-leucine) gave the lowest (run 23). A similar tendency was also observed in the case of type B and C electrodes consisting of platinum base (runs 25–27, 29, 35, and 37). In the oxidation on A_{11}, B_{11}, and C_{11} electrodes, a lower anodic potential (1.8 V vs. Ag/AgCl, runs 20, 24, and 28) resulted in lower optical yields. When the concentration of dip-coating solutions of poly(L-valine) for making C_{11} electrodes was changed in a range of 1.0–0.10% w/v (runs 29, 31, 32, and 34), a maximum optical yield (93%, run 32) was obtained by using a C_{11} electrode coated in 0.25% w/v solution. The optical yield of 93% was also the highest value obtained in not only this work but also previous work[20–29] dealing with electrochemical asymmetric induction. The highest optical yield of the chemical oxidation of **1e** to **2e** had been reported to be 75% for the hydrogen peroxide oxidation in the presence of bovine serum albumin.[18] Higher temperature (run 30) and water content (run 33) decreased optical yields. Graphite was less suitable for the base electrode (runs 36 and 38) than platinum.

In the oxidation of cyclohexyl phenyl sulfide (**1f**), electrodes coated with poly(γ-benzyl L-glutamate) gave almost the same optical yields (runs 40, 43, and 46) as those coated with poly(L-valine) (runs 39, 42, and 45), while poly(L-leucine)-coated electrodes gave lower optical yields (runs 41, 44, and 47).

Optical yields for the oxidation of cyclohexyl *p*-tolyl sulfide (**1g**) (runs 48–56) were lower than those for the oxidation of **1f**.

Results obtained would lead to some general tendencies: (a) optical yields are greatly affected by substituent groups of sulfides, (b) the best type of electrodes is type C, (c) the best poly(amino acid) for coating is poly(L-valine), (d) the concentration of dip-coating solutions of poly(L-valine), i.e., the thickness of poly(L-valine) films, is one of influential factors on the optical yield, and (e) the optical yield is also affected by anodic potential, temperature, and water content of electrolytic solutions.

Although the above tendencies are apparently clear, it may be considerably difficult to rationalize them. Occurrence of asymmetric induction should be caused by stereochemical interaction between inducing reagents (poly(amino acid)s) and prochiral substrate molecules and/or their oxidative intermediates. However, electrochemical oxidation mechanism of sulfides has not been verified at all in terms of not only stereocontrol tendencies but also general tendencies. Among the above tendencies, (a) and (e) are commonly found in electrochemical and chemical asymmetric syntheses. Item b seems very interesting. Tight adhesion of optically active polymer layers on a base electrode should be important for asymmetric induction. Such an adhesion could be achieved by binding covalently the polymer to the electrode in asymmetric reduction on poly(amino acid)-coated graphite cathodes.[26] In the case of type C electrodes, the polypyrrole layer should be more tightly coated than in type B, and also affinity of poly(amino acid)s between the polypyrrole layer may be stronger than that between bare platinum or graphite surfaces in the case of type A electrodes. This may be a reason type C was the best. Items c and d are also interesting. These had been discussed somewhat in detail in an earlier paper[24] dealing with the electrochemical asymmetric reduction of citraconic acid.

Durability of Poly(amino acid)-Coated Electrodes: Reuse of the Electrodes. Although electrodes for electrosyntheses should be durable, poly(amino acid)-coated graphite electrodes were insufficiently durable in the asymmetric reduction of citraconic

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[30] More detailed structures of the platinum electrodes coated with poly(L-valine) (corresponding to A_{11}, B_{11}, and C_{11} electrodes in Figure 1) are shown in a previous report.[29]

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Table I. Asymmetric Oxidation of Alkyl Aryl Sulfides (**1a-g**) to the Corresponding Sulfoxides (**2a-g**) on Poly(amino acid)-Coated Electrodes

				sulfoxide (**2**) formed			
run[a]	starting sulfide	electrode[b]	anodic potential, V vs. Ag/AgCl	current efficiency,[c] %	chem yield,[c,d] %	opt yield,[e] %	abs config[f]
1[g]	**1a**	A_{11}	1.5	60	*h*	1	*S*
2	**1a**	A_{11}	1.8	64	*h*	1	*S*
3[i]	**1a**	A_{11}	1.5	100	100	1	*S*
4	**1a**	A_{21}	1.5	76	*h*	2	*S*
5	**1a**	A_{31}	1.5	82	*h*	2	*S*
6[j]	**1a**	B_{11}	1.5	22	*h*	1	*S*
7	**1a**	B_{21}	1.5	38	*h*	2	*S*
8	**1a**	B_{31}	1.5	32	*h*	2	*S*
9	**1b**	A_{11}	1.9	29	*h*	28	*S*
10	**1b**	B_{11}	1.9	20	*h*	49	*S*
11	**1b**	C_{11}	1.9	27	71	73	*S*
12	**1b**	C_{11}[k]	1.9	19	56	77	*S*
13	**1c**	A_{21}	1.7	44	*h*	6	*S*
14	**1c**	B_{21}	1.7	14	*h*	18	*S*
15	**1c**	B_{22}	1.8	9	*h*	20	*S*
16	**1d**	A_{11}	1.9	16	*h*	16	*S*
17	**1d**	B_{11}	1.9	20	*h*	24	*S*
18	**1d**	C_{11}	1.9	18	55	30	*S*
19	**1d**	C_{11}[k]	1.9	27	69	44	*S*
20	**1e**	A_{11}	1.8	20	59	25	*S*
21	**1e**	A_{11}	2.0	17	57	34	*S*
22	**1e**	A_{21}	2.0	17	*h*	19	*S*
23	**1e**	A_{31}	2.0	15	*h*	7	*S*
24	**1e**	B_{11}	1.8	14	61	58	*S*
25	**1e**	B_{11}	2.0	15	50	66	*S*
26	**1e**	B_{21}	2.0	10	48	30	*S*
27	**1e**	B_{31}	2.0	9	45	10	*S*
28	**1e**	C_{11}	1.8	18	46	79	*S*
29	**1e**	C_{11}	2.0	19	53	86	*S*
30[l]	**1e**	C_{11}	2.0	14	47	55	*S*
31	**1e**	C_{11}[m]	2.0	11	48	50	*S*
32	**1e**	C_{11}[k]	2.0	15	45	93	*S*
33[n]	**1e**	C_{11}[k]	2.0	39	91	59	*S*
34	**1e**	C_{11}[o]	2.0	23	61	65	*S*
35	**1e**	C_{21}	2.0	11	46	35	*S*
36	**1e**	C_{22}	2.1	8	*h*	12	*S*
37	**1e**	C_{31}	2.0	16	62	15	*S*
38	**1e**	C_{32}	2.1	8	*h*	3	*S*
39	**1f**	A_{11}	1.9	34	*h*	28[p]	−54.0°[q,r]
40	**1f**	A_{21}	1.8	16	*h*	26[p]	−51.2°[q,r]
41	**1f**	A_{31}	1.8	31	*h*	17[p]	−33.5°[q,r]
42	**1f**	B_{11}	1.9	15	*h*	40[p]	−81.1°[q,r]
43	**1f**	B_{21}	1.8	13	*h*	42[p]	−82.7°[q,r]
44	**1f**	B_{31}	1.8	15	*h*	37[p]	−72.9°[q,r]
45	**1f**	C_{11}	1.9	31	*h*	54[p]	−106.2°[q,r]
46	**1f**	C_{21}	1.8	28	*h*	51[p]	−100.5°[q,r]
47	**1f**	C_{31}	1.8	26	*h*	41[p]	−80.8°[q,r]
48	**1g**	A_{11}	1.9	38	*h*	10[p]	−18.6°[q,r]
49	**1g**	A_{21}	1.9	28	*h*	7[p]	−13.3°[q,r]
50	**1g**	A_{31}	1.8	29	*h*	5[p]	−9.5°[q,r]
51	**1g**	B_{11}	1.9	35	*h*	17[p]	−32.3°[q,r]
52	**1g**	B_{21}	1.9	30	*h*	7[p]	−13.8°[q,r]
53	**1g**	B_{31}	1.8	26	*h*	12[p]	−22.8°[q,r]
54	**1g**	C_{11}	1.9	31	*h*	22[p]	−41.8°[q,r]
55	**1g**	C_{21}	1.9	33	*h*	18[p]	−34.2°[q,r]
56	**1g**	C_{31}	1.9	37	*h*	16[p]	−30.4°[q,r]

[a] Electrolysis was carried out by passing 2.0 F/mol of charge in acetonitrile containing 1.0% (v/v) of water at 0 °C, unless stated otherwise. [b] Electrode was coated in 0.5% (w/v) of dip-coating solution of amino acids, unless stated otherwise. [c] For total of the enantiomeric products. [d] Based on sulfide consumed. [e] Percentage of enantiomeric excess. [f] For the excess enantiomer. [g] 1.4 F/mol of charge was passed. [h] Not estimated. [i] 10% (v/v) water. [j] 0.9 F/mol of charge was passed. [k] 0.25% (w/v) dip-coating solution. [l] Electrolysis was carried out at 20 °C. [m] 1.0% (w/v) dip-coating solution. [n] 5.0% (v/v) water. [o] 0.10% (w/v) dip-coating solution. [p] Calculated from NMR spectra measured in the presence of an enantiomer-shift reagent. [q] $[\alpha]^{20}{}_{D}$ value measured in acetonitrile. [r] No literature gives absolute configuration.

acid and their asymmetry inducing powers were completely lost after a few times of reuse.[24] As shown in Figure 2 (curve 1), an A_{11} electrode prepared in this work also lost the inducing power when reused repeatedly.

In this work, the durability of poly(L-valine)-coated platinum electrodes was improved first by coating poly(L-valine) after precoating the platinum base with polypyrrole (B_{11} electrode, Figure 2, curve 2). This fact suggests that the affinity of polypyrrole for either platinum or poly(L-valine) is stronger than that of poly(L-valine) for platinum, as described above.

In previous work,[26] it was found that covalently bound polymer layers to the base electrode were much more durable than the corresponding simply dip-coated layers. On this basis, a further improvement of the durability of B_{11} electrode was achieved by binding covalently its polypyrrole layer to the platinum base electrode (C_{11} electrode, Figure 2, curve 3).

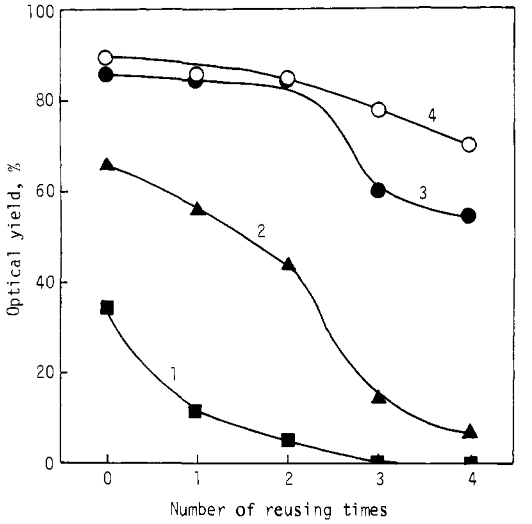

Figure 2. Electrochemical asymmetric oxidation of *tert*-butyl phenyl sulfide (**1e**) to the corresponding sulfoxide (**2e**) on reused poly(L-valine)-coated platinum electrodes. Each electrode was repeatedly reused passing 2.0 F mol^{-1} of charge for each electrolysis in electrolytic solution containing 1% water at a constant current density of 0.3 A dm^{-2} at 0 °C: (1) A$_{11}$ electrode coated in 0.5% w/v coating solution, (2) B$_{11}$ electrode coated in the same, (3) C$_{11}$ electrode coated in the same, (4) C$_{11}$ electrode recoated in 0.25% w/v fresh solution before each electrolysis.

An additional improvement of the durability of the C$_{11}$ electrode in repeated reuse could be made by recoating the electrode in a fresh poly(L-valine) solution after it is rinsed out in trifluoroacetic acid. The durability was somewhat improved by this way and the asymmetry inducing power decreased more slightly with the increase of reusing times, as shown in Figure 2 (curve 4). Such a small decrease of the power may be due to damage of the polypyrrole layer.

Experimental Section

Materials. Sulfide **1a** was commercially supplied from Tokyo Kasei Co. Sulfides **1b–e** and **1f,g** were prepared by the methods of Ipatieff et al.[32] and Zavgorodnii,[33] respectively, and confirmed by boiling point, IR, and MS data.

Poly(amino acid)s (poly(L-valine), poly (γ-benzyl L-glutamate), and poly(L-leucine)) were prepared from the corresponding optically pure amino acids by a method described in our earlier reports.[23,24] Their molecular weights were not known except for poly(L-valine) (ca. 2000[23]).

Poly (amino acid)-Coated Electrodes. The coated electrodes used in this work were prepared by methods similar to those described previously[29] for the preparation of poly(L-valine)-coated platinum electrodes.[30] Before coating, graphite plates were polished with fine emery paper, washed with ethanol, and dried at room temperature.

Electrolysis. The electrolytic oxidation of sulfides was carried out in 0.1 M n-Bu$_4$NBF$_4$/acetonitrile (containing water) by a potentiostatic method. Details of typical electrolytic conditions and procedures were given in the previous report.[29]

Product Analysis. After the electrolysis, the anodic solution was evaporated and then extracted with chloroform. Sulfoxides **2a** and **2b–g** were purely separated from the chloroform extracts by gas chromatography (Triton X305, 200 °C) and column chromatography (Kieselguhr 60), respectively. Eluents for the column chromatography were chloroform (for **2b,d,e**) and chloroform–ethyl acetate (1:1 v/v for **2c**; 9:1 v/v for **2f,g**). The sulfoxides separated thus were confirmed by IR and MS data.

Any products (e.g., sulfones) other than the sulfoxides could not be separated. Oxygen evolution was observed during the electrolysis. Unreacted sulfides were recovered in some cases where chemical yields of the sulfoxides were estimated on the basis of the sulfides consumed.

Optical Yields. Optical rotation of the sulfoxides separated was measured in 1–10-cm photocells of a highly sensitive polarimeter (Union Co. automatic polarimeter, Model PM-101). The optical yields of **2a–e** were calculated with reference to $[\alpha]_D$ values reported for the optically pure enantiomers: $[\alpha]^{20}_D$ + 146.2° (c 1.76, ethanol)[11] for (R)-**2a**, $[\alpha]^{25}_D$ + 169.9° (c 1.6, acetone)[18] for (R)-**2b**, $[\alpha]^{25}_D$ + 178.9° (c 2.0, ethanol)[18] for (R)-**2c**, $[\alpha]^{25}_D$ −237.3° (c 2.0, ethanol)[18] for (S)-**2d**, and $[\alpha]^{25}_D$ + 180.0° (c 2.0, ethanol)[11] for (R)-**2e**. Optical rotation of **2f,g** was also measured in acetonitrile. However, their optical yields were calculated not from their optical rotating powers but from NMR spectra measured in chloroform-d in the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-d-camphorato]europium(III) as an enantiomer-shift reagent. On the basis of the optical rotation and the NMR spectra, we concluded that optically pure **2f** and **2g** have $[\alpha]^{20}_D$ 196.7° (c 2.0, acetonitrile) and $[\alpha]^{20}_D$ 190.0° (c 2.0, acetonitrile), respectively.[34]

Registry No. 1a, 100-68-5; **1b**, 3019-20-3; **1c**, 1126-80-3; **1d**, 13307-61-4; **1e**, 3019-19-0; **1f**, 7570-92-5; **1g**, 3699-01-2; **2a**, 18453-46-8; **2b**, 80225-50-9; **2c**, 77448-93-2; **2d**, 72174-22-2; **2e**, 62076-10-2; **2f**, 89066-10-4; **2g**, 89066-11-5; poly(L-valine), 25609-85-2; poly(L-leucine), 25248-98-0; poly(γ-benzyl L-glutamate), 25014-27-1; platinum, 7440-06-4; graphite, 7782-42-5; polypyrrole, 30604-81-0.

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(34) Relations between the optical rotating powers and optical purities indicated straight lines that coincided the origin.

Polymerizations of Acetylenes and Cyclic Olefins Induced by Metal Carbynes

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Abstract: *trans*-Bromotetracarbonyl(phenylmethylidyne)tungsten and related metal carbynes induce acetylenes and cycloalkenes to polymerize. The acetylenes include examples that are monosubstituted, disubstituted, and unsubstituted, as well as the first reported functionalized acetylenes in which the functional groups (the nitrile, ester, and halogen functions were studied) are not attached to the triple bond. The cycloalkenes yield polyalkenamers whose double bonds are largely cis. This last polymerization is speeded by the presence of oxygen. The stereochemistries of the polyacetylenes and the polynorbornenamer produced when the initiator is the metal carbyne are similar to those of the polymers produced when the initiator is pentacarbonyl(methoxyphenylmethylene)tungsten. A possible mechanism is presented to account for why the metal carbynes behave as though they were sources of reactive metal carbenes.

Ideas about the mechanism of the metal-catalyzed metathesis of olefins[1] suggested that isolable metal carbenes might initiate such reactions, as indeed turned out to be true, as Casey's pentacarbonyl(diphenylmethylene)tungsten[2] (**1**) initiating metatheses

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