Use of Functionalized Ethylene Oligomers To Prepare Recoverable, Recyclable Nickel(0) Diene Cyclooligomerization Catalysts

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Polyethylene-bound alkyl diaryl and triaryl phosphites that act as ligands for homogeneous nickel(0) butadiene cyclooligomerization catalysts are described. The homogeneous nickel(0) catalysts prepared in the presence of these ligands are shown to have the same product selectivity and reactivity as similar nickel catalysts prepared from low molecular weight phosphite ligands in reactions carried out at 100 °C. By varying the ligand/nickel ratio, it is possible to vary the product selectivity of these polyethylene-bound nickel(0) catalysts. High product selectivities (>90%) for 1,5-cyclooctadiene are attainable. These ethylene oligomer ligated nickel(0) catalysts take advantage of the temperature-dependent solubility properties of polyethylene in order to maintain catalyst homogeneity at 100 °C during the oligomerization. Recovery and recycling of the catalyst is possible because the catalyst and polyethylene quantitatively coprecipitate on cooling the reaction mixture to 25 °C.

Nickel(0) complexes catalyze a variety of carbon–carbon bond-forming reactions using dienes, alkenes, and alkynes as substrates.[1] In a preliminary report, we described reactions using functionalized ethylene oligomers as ligands for Ni(0) catalysts.[2] This paper provides details about both the synthesis and use of these catalysts. These studies demonstrate that polyethylene ligands can be used both to recycle a reactive catalyst several times and to achieve high catalyst activity. Equally important, comparison of the results of reactions using these macromolecular polyethylene-like ligands and low molecular weight ligands demonstrates that these recoverable catalysts have variable product selectivity that is directly comparable to that attained with conventional homogeneous catalysts.

Triaryl phosphite complexes of Ni(0) catalyze cyclooligomerization of butadiene to 1,5-cyclooctadiene (COD) with high product selectivity at 80–110 °C in hydrocarbon solutions.[1] The reaction reportedly proceeds through a bis(π-allyl)nickel intermediate.[3] The Ni(0) catalyst is normally prepared in situ by reduction of nickel(II) salts with an alkylaluminum reagent. Using hindered triaryl phosphite ligands like tris(*o*-biphenylyl) phosphite, such catalysts form cyclooligomers like 1,5-cyclooctadiene (COD) with a product selectivity of >90%. Other cyclodimers form in minor amounts and cyclotrimerization or polymerization does not occur to a large extent. Product selectivities in these oligomerization reactions vary significantly with the nature of the ligand and with the ligand/metal ratio.[4] The reported changes in product selectivity as a function of ligand structure and/or concentration are presumably the result of the many possible complexes that can form. These various complexes are in mobile equilibria in these catalyst solutions. As a result, changing the ligand/metal ratio can be used in homogeneous systems in a technique called "inverse titration" to alter or optimize product selectivity.[4] Insoluble phosphorus-containing ligands attached to DVB cross-linked polystyrene have been used to support similar cyclodimerization catalysts.[5] However, Ni(0) catalysts bound to polystyrene do not provide the activity and control over product selectivity available with a conventional soluble hindered triaryl phosphite ligand. While the insolubility of a cross-linked polymeric ligand at the *end* of a reaction facilitates catalyst recovery, the catalyst's insolubility in this case *during* the reaction makes it more difficult to readily control and modify catalyst–ligand interactions. This paper describes in detail soluble macromolecular phosphite ligands that are shown to accurately mimic the chemistry of conventional ligands. These ligands derived from terminally functionalized polyethylene are insoluble at the end of a reaction but are soluble during the reaction. These macromolecular ligands provide greater opportunities for optimization and control of catalyst reactivity and selectivity and at the same time facilitate separation of products and catalyst.

We recently described an alternative to insoluble cross-linked polymers as reagents or catalyst supports.[2,6-9] This approach uses functionalized ethylene oligomers as macromolecular catalyst ligands or reagents. Macromolecular catalysts or reagents derived from ethylene oligomers are usable as homogeneous solutions at elevated temperature. However, on cooling to room temperature, these polyethylene-like reagents, ligands, and catalysts precipitate. The polyethylene semicrystalline matrix entraps the catalyst, ligand, or reagent and separates it from the solution containing the reaction product.[10] This paper describes phosphite-functionalized ethylene oligomers that serve as ligands for Ni(0)-catalyzed butadiene cyclooligomerization reactions. These Ni(0) catalysts are examples of recoverable polymer-bound catalysts that closely resemble homogeneous catalysts in their reactivity and selectivity. The data presented here also shows that varying the ligand to metal ratio and the ligand structure leads to predictable changes in catalyst activity and selectivity.

Results and Discussion

Syntheses of Ligands. Ethylene oligomers containing terminal phosphite ligands were synthesized from hydroxylated ethylene oligomers. The hydroxyl-containing

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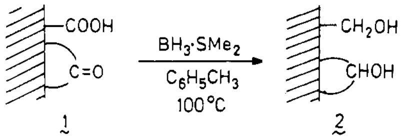
polyethylenes were derived from these different precursors. The most common strategy involved the reduction of polyethylene-containing carboxyl or carbonyl groups using borane–dimethyl sulfide.[11] Commercially available oxidized polyethylene (1) and carboxylated linear ethylene oligomers were both suitable starting materials for these reductions (eq 1–2). Alternatively, hydroxyl-functionalized ethylene oligomers were prepared directly by quenching a "living" ethylene oligomer (3) with ethylene oxide (eq 3).



(1)

$$CH_2{=}CH_2 \xrightarrow{n\text{-BuLi}} -\!\!(-CH_2CH_2-)_n\!-CH_2CH_2Li \xrightarrow{CO_2} \xrightarrow{H^+/H_2O}$$

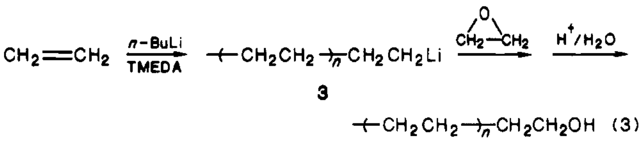
3

$$-\!\!(-CH_2CH-)_n\!-CH_2CH_2COOH \xrightarrow[\text{toluene}]{BH_3\,S(CH_3)_2}$$

4

$$-\!\!(-CH_2CH_2-)_n\!-CH_2CH_2OH \quad (2)$$

5



(3)

$$CH_2{=}CH_2 \xrightarrow[\text{TMEDA}]{n\text{-BuLi}} -\!\!(-CH_2CH_2-)_n\!-CH_2CH_2Li \xrightarrow{CH_2-CH_2\ (O)} \xrightarrow{H^+/H_2O} -\!\!(-CH_2CH_2-)_n\!-CH_2CH_2OH$$

The displacement of an aryloxy group from a triaryl phosphite by the lithium alkoxide formed by *n*-butyllithium deprotonation of hydroxylated polyethylene was the most useful method for synthesis of mixed polyethylene diaryl phosphites like **6a–c** (eq 4). Other pro-

$$-\!\!(-CH_2CH_2-)_n\!-CH_2CH_2OH \xrightarrow{n\text{-BuLi}} -\!\!(-CH_2CH_2-)_n\!-CH_2CH_2OLi \xrightarrow{(ArO)_3P}$$

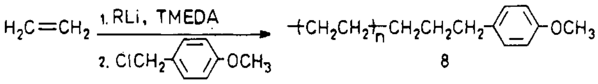
$$-\!\!(-CH_2CH_2-)\!-CH_2CH_2OP(OAr)_2 + LiOAr \quad (4)$$

6a, Ar = C_6H_5
6b, Ar = o-$CH_3C_6H_4$
6c, Ar = o-$C_6H_5C_6H_4$

cedures usually used to make phosphites from alcohols work but are not as general or lead to byproducts. For example, under neutral conditions with azeotropic distillation of ethanol, hydroxylated polyethylene and triethyl phosphite yielded polyethylene diethyl phosphite. However, this procedure does not work with triaryl phosphites. Attempts to prepare oligomeric phosphites from hydroxy-containing ethylene oligomers by displacement of a chlorine from a chlorophosphite also failed. Instead, this reaction produced mixtures of products that included mixed phosphonates as seen from their IR spectra and from their ^{31}P NMR spectra. The reason phosphonate formed instead of the expected phosphite could be due to a rearrangement of the mixed phosphite under the reaction conditions used.[12] Such rearrangements are known to occur in the presence of small amounts of hydrogen phosphite $(RO)_2POH$ or chloride ion at elevated temperatures.

Characterization of the oligomeric phosphites is readily accomplished by both IR spectroscopy and by solution-state ^{1}H and ^{31}P NMR spectroscopy. For example, the polymer prepared from the hydroxylated polyethylene and diphenyl chlorophosphite using triethylamine as a base gave a strong signal at δ 6.5 in its ^{31}P NMR spectrum and strong absorption in the 1260–1200-cm^{-1} region. These results indicate the formation of phosphonate. ^{31}P NMR spectroscopy is a good analytical tool to distinguish between phosphites and phosphonates.[13] The ^{31}P NMR chemical shifts for phosphites are in the range of δ 120–145 whereas the chemical shifts for phosphonates are in the δ 0–40 range. The polymers containing polyethylene diaryl phosphite ligands prepared by either of the above procedures had a signal in their ^{31}P NMR spectra in the region δ 125–135. Various phosphite-functionalized polyethylene and ethylene oligomers prepared in these ways are listed in tabular format in the Experimental Section along with their ^{31}P NMR analytical data. Octadecyl diaryl phosphites **7a–c** were also prepared from octadecanol and used as models for the phosphite functionalized ethylene oligomers. These lower molecular weight analogues were characterized by ^{1}H and ^{31}P NMR spectroscopy and had ^{31}P NMR spectra similar to those of phosphite-functionalized ethylene oligomers with similar substituents (cf. Table II below).

Because of the reactivity of polyethylene diaryl phosphite ligands (vide infra), triaryl phosphite ligands derived from ethylene oligomers containing terminal phenol groups were also prepared. This required linear ethylene oligomers bearing terminal methoxyphenyl groups that were prepared by quenching lithiated ethylene oligomers **3** obtained by anionic polymerization of ethylene with 4-methoxybenzyl halides (eq 5).[14] Methoxyphenyl-functionalized alkene oligomers **8** were demethylated by using $ISi(CH_3)_3$ to form phenol-terminated alkene oligomers **9**.[15] The phenol-terminated ethylene oligomers were then converted to analogues or triaryl phosphites by deprotonation of the phenol and subsequent displacement of a chloride from a the diaryl chlorophosphite. Polyethylenephenyl diaryl phosphite terminated ethylene oligomers prepared contained bis(*o*-tolyl) and bis(*o*-biphenyl) groups as the other two aryl groups of the triaryl phosphite (**10b** and **10c**). These oligomeric phosphites were characterized by ^{31}P NMR spectroscopy and IR spectroscopy.



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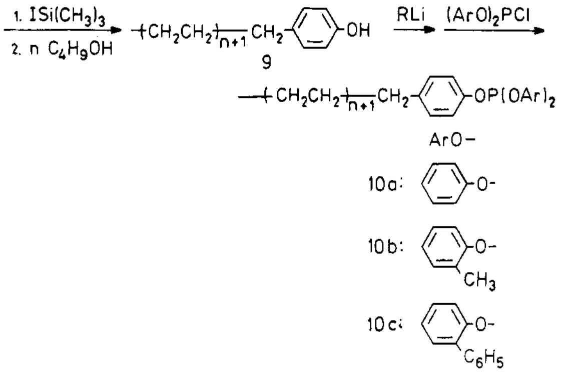

(6)

Catalytic Studies. Nickel(0)-catalyzed cyclooligomerizations of butadiene in the presence of polyethylene-derived phosphites were conducted in toluene at

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Table I. Nickel(0)-Catalyzed Cyclooligomerization of Butadiene in the Presence of Various Phosphite Ligands PE-OP(OAr)$_2$ or PE-C$_6$H$_4$OP(Ar)$_2$[a] (PE = Polyethylene)

			products[b]			
ligand[c]	time, h	convn, %	COD	VCH	CDT	others
12a	5	70	60	14	23	3
6a	4	75	65	12	20	3
6a	4	47[d]	35	45	20	
7a	4	75	68	15	12	5
P(OPh)$_3$	4	85	77	6	15	2
12b	5	70	60	10	24	4
6b	4	85	85	8	5	2
6b	4	60[d]	87	6	7	
7b	4	90	87	10	2	1
10b	5	92	87	8	5	4
10b	5	82[e]	82	10	8	
11b	5	96	90	7	3	3
P(O-*o*-tolyl)$_3$	4	98	90	7	2	1
12c	3	80	89	6	2	2
6c	3	85	92	6	5	2
6c	3	56	80	16	4	
7c	3	86	90	4	6	2
10c	5	95	93	5	2	2
11c	5	97	92	6	2	3
P(OBP)$_3$	3	96	95	3	2	1
P(OBP)$_3$	4	100[e]	96	2	1	

[a] Cyclooligomerizations were carried out at 100 °C in toluene with 0.25 mmol of Ni(0), 0.25 mmol of P(OAr)$_2$ and a Ni/butadiene ratio (mmol/mmol) of 1:200 or greater. [b] COD stands for 1,5-cyclooctadiene, VCH stands for 4-vinylcyclohexene, and CDT stands for (*E*,*E*,*E*)-1,5,9-cyclododecatriene. Other refers to nonoligomeric products. [c] The type of ligand used and its preparation is described in detail in the Experimental Section. [d] The extent of conversion and the product selectivities after three cycles (total turnover of ca. 1100 mmol product/mmol Ni). [e] Taken from ref 2. BP stands for *o*-biphenylyl.

100 °C. Typically, a 3-fold excess of a 1 M hexane solution of Al(Et)$_3$ was added to a fine suspension of 0.2 mmol of Ni(acac)$_2$ and an oligomeric phosphite like **6** (0.5 g, 0.5 mmol of (POAr)$_2$ g^{-1} of polymer) in a mixture of toluene and butadiene (150 mmol). The resulting amber suspension was heated to 100 °C in a heavy glass pressure vessel to give an amber solution. After the solution had formed (95 °C), oligomerization ensued as evidenced by the drop in pressure caused by the consumption of butadiene. The reactions were normally complete in 3–5 h. The above reactions were then compared with similar cyclooligomerizations conducted in the presence of corresponding octadecanol-derived mixed phosphites **7a–c**. The results of these studies are presented in Table I.

The results shown in Table I clearly show that the use of functionalized ethylene oligomer bound ligands for Ni(0) catalysts leads to product selectivities and catalyst activities that are very close to those obtained by using an octadecyl diaryl phosphite ligand. Changing the structure of the groups of the oligomeric phosphite ligands leads to the same changes in product selectivities as are seen when the identity of the low molecular weight phosphite is similarly changed. Furthermore, the changes in product selectivities parallel those reported for low molecular weight symmetrically substituted phosphites. For example, the selectivity for 1,5-cyclooctadiene increased with the steric bulk of the polyethylene diaryl phosphite used. The highest selectivity (>95%) for 1,5-cyclooctadiene formation was achieved for polyethylene bis(*o*-biphenylyl) phosphite. The selectivities for the cyclodimer product 1,5-cyclooctadiene seen when these oligomeric phosphite ligands were used were still lower than for the corresponding triaryl phosphites. This is probably because of the replacement of one aryl group by an alkyl group in the ethylene oligomer derived phosphites. Presumably, the steric bulk around the alkyl diaryl phosphites is smaller than that in triaryl phosphites.

Table II. ^{31}P NMR Spectral Data for Polyethylene Diaryl Phosphites [PE-O(OAr$_2$)$_2$] and Polyethylenephenyl Diaryl Phosphites [PE-C$_6$H$_4$OP(OAr)$_2$][a] (PE = Polyethylene)

ligand	alkyl moiety (PE)	Ar =	^{31}P chemical shift[b]
12a	polyethylene[c]	phenyl	130–133
12b		*o*-tolyl	129
12c		*o*-biphenylyl	128
6a	ethylene oligomer[d]	phenyl	130
6b		*o*-tolyl	129
6c		*o*-biphenylyl	128
7a	*n*-C$_{18}$H$_{37}$	phenyl	130
7b		*o*-tolyl	128
7c		*o*-biphenylyl	128
10b	ethylene oligomer[d]	*o*-tolyl	129
10c		*o*-biphenylyl	129
11b	*n*-C$_{19}$H$_{39}$	*o*-tolyl	128.5
11c	*n*-C$_{19}$H$_{39}$	*o*-biphenylyl	129

[a] NMR spectra were recorded at 100 °C in toluene on an FT-80 NMR spectrometer at 32.2 MHz. [b] Chemical shifts are in ppm and are relative to 85% H$_3$PO$_4$ (external). [c] Polymer preparation starting from commercially obtained oxidized polyethylene. [d] Linear ethylene oligomers obtained by anionic oligomerization of ethylene (M_v, 1800).

The use of functionalized ethylene oligomers as ligands allows recovery of the active nickel(0) catalyst as a dispersion in a polyethylene precipitate on cooling.[16] Occasionally, the supernatant solution from the first reaction cycle was light yellow, indicating some leaching of nickel. This may be the excess nickel in the initial charge that was not be complexed to the oligomeric phosphite as the Ni to phosphite ratio was maintained at 1:1 in these studies. However, in subsequent cycles, the supernatant solution containing the organic products was always colorless. The light yellow precipitate containing the catalyst was washed with dry toluene. It could then be reused in a cyclooligomerization with a fresh charge of toluene and butadiene. No additional alkylaluminum reagent was added or needed. The results from the recycling of these catalysts are presented in Table I. As can be seen, catalytic activity

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[16] The identity of the actual Ni(0) species recovered was not studied but it evidently includes a oligomeric phosphite ligand or else it would not have been trapped (cf. ref 10).

is retained at least through three recycles in most of the catalyst systems. Analysis of supernatant solution from the second recycle of a cyclodimerization showed that much less than 0.1% of the original nickel was lost to solution. Thus, little or no nickel catalyst is lost in these recycling procedures.

Control experiments using octadecyl diaryl phosphites as ligands in the presence of virgin polyethylene demonstrated the importance of a polyethylene-like macromolecular ligand in catalyst recycling. Less than 1% of the original catalytic activity was present when a second reaction cycle was carried out using this lower molecular weight phosphite ligand. The implication that entrapment and consequent catalyst recovery requires a polyethylene-like macromolecular ligand is in accord with earlier studies from our group on entrapment functionalization.[10]

No reactivation of the catalyst was necessary up to the point where the product selectivity began to change considerably. At this point, the activity and the selectivity were restored somewhat by addition of $Al(Et)_3$; however, the activity and selectivity could not be restored to their original levels. This could be the result of many factors. Nickel(0) is an extremely moisture- and oxygen-sensitive species. Repeated recovery and recycling operations might have adventitiously oxidized this catalyst. A more likely explanation though is that the phosphite ligands derived from hydroxyl-functionalized ethylene oligomers decomposed or rearranged. For example, ester interchange of these mixed phosphites could have led to formation of a bis(polyethylene) aryl phosphite or a tris(polyethylene) phosphite. Alternatively, some phosphonate could have formed as mentioned before. Experiments in which polyethylene diaryl phosphite ligands were heated in toluene for extended periods of time indicated that irreversible changes in the ligands did occur based on ^{31}P NMR spectroscopy. For example, the ethylene oligomer phosphite carrying the *o*-biphenylyl group initially had a signal at δ 128 in its ^{31}P NMR spectrum at 100 °C. After heating this ligand at 110 °C for 72 h, resonances were seen at δ 6 and at δ 130. The signal at δ 6 corresponds to a phosphonate species and the signal at δ 130 corresponds to that of a trialkyl phosphite. Additional evidence for the instability of the phosphite ligands came from experiments using mixed polyethylene diaryl phosphites derived from what originally was commercial oxidized polyethylene. In this case, a gel formed on prolonged heating. In this case, the ester interchange of the polyethylene diaryl phosphite between the polyfunctional chains resulted in cross-linking and formation of a polymer gel.

In an effort to circumvent this problem of ester interchange, we prepared polyethylene phenyl diaryl phosphite ligands **10**. Nickel(0)-catalyzed cyclooligomerizations of butadiene carried out in the presence of either the polyethylenephenyl or corresponding low molecular weight model nonadecylphenyl diaryl phosphites **11** were homogeneous at 100 °C as expected. However, although the product selectivity favoring 1,5-cyclooctadiene was slightly improved (Table I) through three cycles, ligand decomposition remained a problem. Recycling the catalyst beyond three cycles still led to decreased activity and/or selectivity. In some cases, ligand decomposition was evidenced by the formation of a Ni(0) precipitate. Adventitious disproportionation, oxidation or other reactions of these polymeric catalyst ligands is a problem if these Ni(0) catalysts are to be recycled many times.[17]

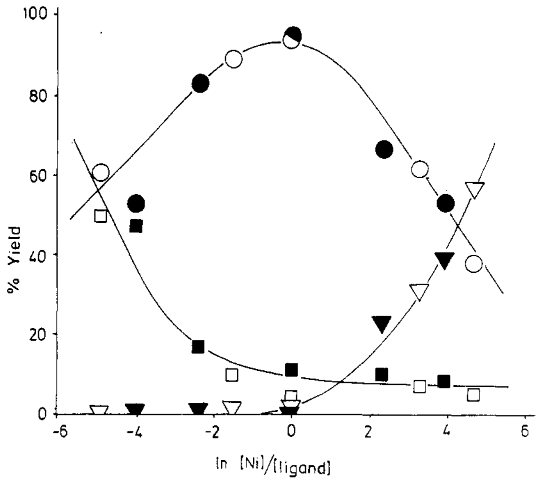

Figure 1. Plot of catalyst selectivity vs. ln ([Ni]/[phosphite ligand]) for nickel(0)-catalyzed cyclooligomerization of butadiene in the presence of various alkyl diaryl phosphite ligands. Product yields using polyethylenephenyl bis(*o*-tolyl) phosphite (**10b**) as ligand: (○) 1,5-cyclooctadiene; (□) (*E,E,E*)-1,5,9-cyclododecatriene; (▽) 4-vinylcyclohexene. Product yields using nonadecylphenyl bis(*o*-tolyl) phosphite (**11b**) as a ligand: (●) 1,5-cyclooctadiene; (■) (*E,E,E*)-1,5,9-cyclododecatriene; (▼) 4-vinylcyclohexene.

Optimization of a homogeneous catalyst's activity and selectivity through alteration of ligand structure or by variation of the ligand/metal ratio has proven to be a useful advantage of homogeneous catalysts. Unlike insoluble polymer-bound catalyst ligands, these soluble macromolecular catalyst ligands are as useful as low molecular weight ligands in this regard. For example, varying the ligand/metal ratio in these nickel(0)-catalyzed cyclooligomerization reactions is known is known to change the product selectivity. Product selectivity vs. log (ligand/metal) maps called the "inverse titration" curves were obtained for the phosphite-functionalized ethylene oligomer ligand **10b** and were compared to a similar map prepared by varying the model phosphite ligand **11b**. These results are presented in Figure 1. Using *o*-tolyl-functionalized ethylene oligomer **10b**, the product selectivity varied with the change in Ni to ligand ratio in a similar manner to the product selectivity changes obtained by using the 4-nonadecylphenyl bis(*o*-tolyl) phosphite (**11b**). For example, the highest selectivity for 1,5-cyclooctadiene was obtained when the Ni to ligand ratio was 1:1 using either triaryl phosphite functionalized ethylene oligomer or the small molecular analogue **11b**. Very similar variation is also seen for vinylcyclohexene and cyclododecatriene over the range of Ni/ligand ratio studied. This strongly suggests that the ligand environment provided by the triaryl phosphite functionalized ethylene oligomers is similar to the homogeneous analogues.

Conclusion. The use of phosphite-functionalized ethylene oligomers as ligands for Ni(0)-catalyzed cyclooligomerization allows the reaction to be conducted under homogeneous conditions at 100 °C and also allows the separation and recovery of the active catalyst entrapped in a precipitate of ethylene oligomer at room temperature. The quantitative recovery of the Ni(0) catalyst in its active form allows for its recycling through several cycles without the need for reactivation of the catalyst. Further, the homogeneity of these functionalized ethylene oligomers at the reaction temperature allows product selectivities, reaction rates, and variation in product selectivities with changes in the ligand to metal ratio attainable with conventional homogeneous ligands. The major limitation to more extended recycling of these homogeneous catalysts is the instability of the hindered di- and triaryl phosphite

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[17] Ligand decomposition may be a general limiting factor in homogeneous catalysis, cf: Garrou, P. *CHEMTECH* **1985**, *15*, 123–125.

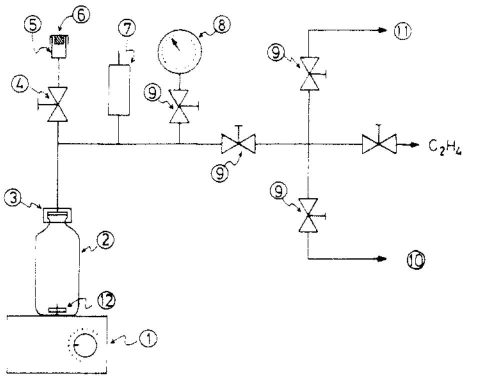

Figure 2. Apparatus used for anionic polymerization of ethylene and butadiene oligomerization reactions: (1) magnetic stirrer; (2) Lab Crest pressure bottle; (3) pressure coupling; (4) 3-mm bore ball valve; (5) 12-mm charging port; (6) rubber septum; (7) safety valve; (8) pressure guage; (9) needle valve; (10) Firestone valve (Ace Glass); and (11) magnetic stirring bar. For butadiene oligomerizations, a source of butadiene replaced the source of ethylene.

ligands that are needed to attain high selectivity in cyclooligomerizations using these nickel(0) catalysts.

Experimental Section

General Methods. Air- and moisture-sensitive reactions were carried out by using standard inert atmosphere techniques.[18] Tetrahydrofuran (THF), heptane, cyclohexane, di-*n*-butyl ether, and toluene were purified by distillation from sodium benzophenone ketyl under an atmosphere of nitrogen. Other solvents were reagent grade and were used as such. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was purified by distillation from potassium metal and kept over potassium metal under argon. Ethylene, carbon dioxide, and hydrogen were purchased as chemically pure grade gases from either Matheson or Airco Gas Co. and were used as obtained. *n*-Butyllithium was obtained from Aldrich Chemical Co. as hexane solutions that were titrated before use.[19] Diarylchlorophosphites and triaryl phosphites were prepared by literature procedures.[20] High molecular weight oxidized polyethylene was purchased from Aldrich Chemical Co. and had a carboxyl content of 0.5 mequiv of CO_2H g^{-1} of polymer. Ethylene oligomerizations and cyclooligomerizations of butadiene were carried out in pressure aerosol test bottles obtained from Lab Crest Scientific, Warminster, PA 18974. A schematic drawing of the apparatus used for these reactions is shown in Figure 2.

Analytical and Spectroscopic Methods. Volatile products from reactions were analyzed on a Hewlett-Packard 5830A gas chromatograph using a 1.8-m OV-17 column and the products were further characterized by GC-MS using a Hewlett-Packard 5970A GC/MS system. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer and ^1H NMR spectra of polyethylene samples were obtained in either cyclooctane or toluene-d_8 solutions with hexamethyldisiloxane (HMDS) as an internal standard at 105–110 °C. Typically NMR samples contained between 0.40 to 0.50 g of polymer as a ca. 25% weight percent solution. ^{31}P NMR spectra were recorded on a Varian FT-80 spectrometer. The chemical shifts reported for ^1H are relative to Me_4Si and the ^{31}P NMR chemical shifts were reported relative to H_3PO_4 (external) and are reported in ppm. IR spectra of polyethylenes were recorded as KBr pellets or thin films obtained by compressing the powder in a 13-mm diameter die press.

Preparation of Functionalized Ethylene Oligomers by Anionic Polymerization. Anionic oligomerization was accomplished according to a literature procedure.[21] The living oligomers so obtained were then transformed into hydroxylated polymers either by carboxylation followed by borane–dimethyl sulfide reduction or by quenching the living oligomer with ethylene oxide. Anionic oligomerizations were carried out such that the product oligomer had a M_v of >1200 so that the product ligand would have the desired temperature-dependent solubility and be entrappable in polyethylene.

Preparation of 4-Methoxyphenyl-Terminated Ethylene Oligomers. The title polymer was made from a batch of lithiated polymer **3** (16 mequiv of *n*-butyllithium initiator). 4-Methoxybenzyl chloride[22] (6 g, 30 mmol) was transferred by a syringe to a stirred suspension of **3** that had been precooled to −78 °C. The resulting suspension was allowed to warm to room temperature and then stirred for 24 h. The reaction mixture was next heated to 115 °C for 12 h. Some of the solids dissolved and the suspension changed color from pale yellow to dark brown. After cooling this mixture to room temperature and releasing any pressure, the suspension was filtered through a coarse-fritted funnel. The solid product was washed several times each with methanol, with 50% aqueous ethanol, and with acetone and finally dried in vacuo. Low molecular weight ethylene oligomers were removed by dissolved this recovered material in hot toluene and isolating the precipitate that formed on cooling the toluene solution. This process was repeated three times. Acetone was added to the precipitate to aid in filtration. The yield obtained was typically 21 g (average of five runs): IR (KBr) cm^{-1} 2900–2800 (br, s), 1610 (br, w) 1530 (sh, w), 1460 (sh, s), 1120 (sh, w), 1080 (sh, w), 720–710 (sh, s); ^1H NMR (cyclooctane, 100 °C) δ 6.9 (4 H, q) and 3.6 (3 H, s). The polymer had a p-$MeOC_6H_4$ loading of 0.55 mmol g^{-1} of polymer.

Demethylation of 4-Methoxyphenyl-Terminated Ethylene Oligomers. A magnetic stirring bar and 2 g of the methoxyphenyl-terminated ethylene oligomer above were placed in a clean, dry 100-mL round-bottomed flask equipped with a reflux condenser under argon. Freshly distilled *n*-heptane was added along with 1 mL of freshly distilled $ISi(CH_3)_3$ and the resulting suspension was heated to 95 °C. After being heated at 95 °C for 90 h, the solution was cooled and 1-butanol (5 mL) was added. Heating to 95 °C then decomposed the silylated product. Centrifugation of the suspension that formed on cooling this reaction mixture yielded a solid that was washed twice with 95% ethanol (50 mL) and then heated as a suspension in 20 mL of 95% ethanol containing 5 mL of 10% HCl to 80 °C for 12 h. Cooling yielded a precipitate that was washed with distilled water until the washings were neutral. The polymer was dried in vacuo to yield 1.9 g of a white powder: IR (film) cm^{-1} 1610 (sh, s), 1520 (sh, s), 110–1080 (b, m), 805 (b,m); ^1H NMR (cyclooctane, 110 °C) δ 6.9 (m). A small singlet at δ 3.6 in the ^1H NMR spectrum indicated that 5% unreacted methoxyphenyl oligomer remained in what was now a phenol terminated oligomer.

Preparation of 4-Nonadecylphenol. (1-Methoxy-4-nonadecyl)benzene was prepared by reaction of a copper(I) reagent derived from methylcopper(I) and (4-methoxyphenyl)magnesium chloride and 1-iodooctadecane in a variation of a literature procedure.[23] The methyl ether so obtained was demethylated by using iodotrimethylsilane to yield the desired product, 4-nonadecylphenol. Recrystallization of the crude product from 95% ethanol yielded a total of 13 g (98%) of product: mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 6.9 (d, d, 4 H) 5.6 (br, s, 1 H), 2.7 (dt, 2 H), 1.5–1.11 (m, 34 H), 0.9 (t, 3 H); IR (KBr) cm^{-1} 3400 (br), 2900, 2850, 1610, 1601, 1505, 1440, 1380, 1260 (s, COH), 1160, 1100, 820, and 710.

General Procedure for the Preparation of Chlorophosphites. Monochlorophosphites of ethyl, phenyl, and *o*-tolyl groups represented by the general formula $(RO)_2PCl$ were made by literature procedures.[20] Bis(*o*-biphenylyl) chlorophosphite, $ClP(O\text{-}o\text{-}C_6H_5C_6H_4)_2$, was made as follows. Dry, powdered 2-phenylphenol (17 g, 0.1 mol) was placed in a 250-mL, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser. The system was flushed with nitrogen for 5 min and PCl_3 (5 mL, 7.5 g, 55 mmol) was added. The top of the condenser was fitted with a drying tube containing anhydrous $CaCl_2$ and

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Drierite. The mixture was heated in an oil bath at 120 °C for 6 h to give a light amber solution. At the end of the reaction, the solution was cooled and the reflux condenser was replaced with a single-piece vacuum distillation set-up. Unreacted PCl_3 was removed under reduced pressure and the viscous oily residue was distilled to yield the desired monochlorophosphite (12 g, bp 228–235 °C, 0.2 torr): ^{31}P NMR (toluene) δ 163.0; ^1H NMR ($CDCl_3$) δ 7.7 (m, 4 H), 7.1 (m, 5 H); IR (neat) cm^{-1} 3080–3010 (sh, m), 1605–1590 (sh, m), 1500 (sh, m), 1480 (sh, s), 1430 (sh, s), 1250 (sh, m), 1180 (br, s), 1110 (sh, s), 1050 (sh, s), 920–890 (br, s), 760–730 (br, s), 700 (sh, s). Lower and higher boiling impurities were the dichlorophosphite and the triaryl phosphite, which had peaks in their ^{31}P NMR spectra at δ 182 and 128, respectively.

Preparation of Octadecyl Diaryl Phosphites 7a–c. Octadecyl diaryl phosphites of general formula $C_{17}H_{35}CH_2OP(OAr)_2$ where Ar = phenyl, *o*-tolyl, and *o*-biphenylyl groups were all prepared by the general method described below for the preparation of octadecyl diphenyl phosphite. Octadecanol (5 g, 18.5 mmol), dry THF (60 mL), and a magnetic stirring bar were placed in a dry 250 mL, round-bottomed flask. The flask was fitted with a condenser and connected to an argon bubbler. The solution of the alcohol was cooled in an ice bath and a 1.1 N solution of methyllithium in ether (17 mL, 18.5 mequiv) was added slowly with a syringe. The lithium salt of the alcohol was an insoluble gel at this stage. The suspension was allowed to warm to room temperature to give a clear solution that was stirred for 30 min. This solution was cooled to −10 °C and triphenyl phosphite (12 g, 39 mmol) was added with vigorous stirring. The solution was allowed to warm to room temperature and heated to 50 °C for 3 h. At the end of the reaction, the solution was allowed to cool to room temperature and the solvents were removed under reduced pressure. Addition of dry heptane (250 mL) to the resulting thick syrupy liquid gave a copious white precipitate of the lithium phenoxide. The supernatant after centrifugation was isolated and concentrated under reduced pressure to yield a clear oily residue. Chromatography on a neutral alumina column (50 g, 1-m long, 30-mm diameter) and elution with hexane yielded 8.6 g (92%) of octadecyl diphenyl phosphite: ^{31}P NMR (toluene) δ 130; ^1H NMR (dioxane) δ 6.9 (m, 10 H), 3.9 (t, 2 H), 1.3 (s, br, 31 H), 0.9 (t, 3 H); IR (neat) cm^{-1} 2900–2800, 1615, 1450, 1350, 1230, 1110, 1030, 880, and 715.

Preparation of 4-Nonadecylphenyl Bis(*o*-tolyl) Phosphite (11b). The lithium salt of 4-nonadecylphenol was prepared on a 5.5-mmol scale is described above. Then bis(*o*-tolyl) chlorophosphite (1.9 g, 6.7 mmol) was added to this solution of lithium salt by using a syringe. The resulting solution was stirred at room temperature for 2 h and then warmed to 50 °C. After being stirred at 50 °C for 2 h, the solution was cooled to room temperature and the solvent was removed under reduced pressure. Dry hexane (100 mL) was added and the lithium chloride precipitate that formed was separated from the solution of the phosphite by centrifugation. Solvent hexane was removed under reduced pressure and the oily residue was dried under high vacuum. The crude product (3.2 g, 95%) was purified by column chromatography on alumina as described for the purification of octadecyl diphenyl phosphite (7) above: ^{31}P NMR (toluene) δ 128; IR (neat) cm^{-1} 2900, 2800, 1605, 1590, 1500, 1450, 1390, 1200, 1110, 910, 890, 720, and 710. 4-Nonadecylphenyl bis(*o*-biphenylyl) phosphite (11c) was prepared in the same manner by using bis(*o*-biphenylyl) chlorophosphite and lithium 4-nonadecylphenoxide.

Preparation of Diaryl Phosphite Functionalized Polyethylene and Ethylene Oligomers 12a–c and 6a–c. Phosphites of the general formula $ROP(OAr)_2$ where R is either polyethylene or an ethylene oligomer and Ar is phenyl, *o*-tolyl, or *o*-biphenylyl were prepared by a variation of the general procedure described above using a lithium salt of a hydroxylated polyethylene or ethylene oligomer (2.5 mmol of OLi) and triphenyl phosphite (5 g, 16 mmol) at 60 °C for 6 h with good stirring. At the end of the reaction, the suspension of polymer product was centrifuged and the supernatant was removed. The precipitate was washed with dry THF (50 mL). The supernatant after centrifugation was checked by ^{31}P NMR spectroscopy for the presence of phosphites. After three washes, no phosphite was detected in the washes. Dry THF (100 mL) was added to the final precipitate and the suspension was filtered through a Gelman-Model 4280 pressure filter by using Whatman No. 1 filter paper under an argon pressure (ca. 10 psig). Drying in vacuo overnight yielded 5.1 g of white powder: IR (film) cm^{-1} 2900–2800 (br, s), 1605 (br, m), 1580 (sh, s), 1450 (sh, s), 1380 (s, s), 1220 (sh, s), 1130–1180 (br, s), 1020 (sh, s), 920 (s, w), 780–760 (br, w), 720–710 (sh, s). The preparation of bis(*o*-tolyl) (6b) and bis(*o*-biphenylyl) (6c) derivatives of the ethylene oligomers and polyethylene was very similar to that described above for the diphenyl phosphite of polyethylene. The NMR and IR spectroscopy data for both these derivatives are presented below. Phosphite 6b: ^{31}P NMR (toluene, 100 °C) δ 129. For 6c: δ 128. Phosphite 6b: IR (film) cm^{-1} 1605–1595 (br, w), 1505 (sh, w), 1370 (s, w), 1220 (sh, s), 1030 (sh, s), 910 (sh, w), 760–730 (sh, w). The IR spectrum for 6c was very similar to that of 6b except for absorptions at 1200 (sh, s), 1110 (sh, w), and 880 (br, s) cm^{-1}.

Preparation of 4-Polyethylphenyl Diaryl Phosphites 10b and 10c. Phosphites of the general formula $RC_6H_4OP(OAr)_2$ where R is an ethylene oligomer and Ar is *o*-tolyl or *o*-biphenylyl were prepared by a variation of the general procedure described above for the 4-nonadecylphenyl diaryl phosphites using a lithium salt of a phenol-terminal ethylene oligomer in place of 4-nonadecylphenol. In a typical preparation, 5 g of the starting phenol-containing oligomer was lithiated and the suspension of the lithiated polymer cooled to −78 °C. Bis(*o*-tolyl) chlorophosphite (3g, 10 mmol) was added to this cold suspension by using a syringe. The reaction mixture was first allowed to warm to room temperature and then heated to 60 °C for 6 h with good stirring. At the end of this time, the mixture was cooled to form a suspension that was then centrifuged. Removal of the supernatant yielded a precipitate that was washed with dry THF (50 mL). After three such washes, no phosphite was detected in the supernatant by ^{31}P NMR spectroscopy. THF was added to the final precipitate and the suspension was filtered through a Gelman pressure filter under an argon pressure (ca. 10 psig) as described above to yield, after solvent removal and drying in vacuo overnight, 5 g of a white powder: IR (film) cm^{-1} 2900–2800 (br, s), 1605 (br, m), 1580 (sh, s), 1450 (sh, s), 1380 (s, s), 1220 (sh, s), 1130–1180 (br, s), 1020 (sh, s), 920 (s, w), 780–760 (br, w), 720–710 (sh, s); ^{31}P NMR (toluene, 100 °C) δ 129. The preparation of the bis(*o*-biphenylyl) (10c) phosphite derivative of the ethylene oligomer 37 was very similar. Phosphite 10: ^{31}P NMR (toluene, 100 °C) δ 129; IR (film) cm^{-1} 2900–2800 (br, s), 1600 (br, m), 1580 (sh, s), 1450 (sh, s), 1380 (s, s), 1220 (sh, s), 1130–1180 (br, s), 1020 (sh, s), 920 (s, w), 780–760 (br, w).

General Procedure for Nickel(0)-Catalyzed Cyclooligomerization of Butadiene in the Presence of Phosphite and Phosphine Functionalized Ethylene Oligomers. Nickel(0)-catalyzed cyclooligomerizations in the presence of phosphites of the general formula $ROP(OAr)_2$ where R = ethylene oligomers, polyethylene, or phenol terminated ethylene oligomers and Ar = phenyl, *o*-tolyl, or *o*-biphenylyl, groups were all carried out similarly. A cyclooligomerization reaction using the diphenyl phosphite functionalized ethylene oligomer 6a is described as a typical procedure. In a 100-mL Lab Crest pressure bottle (Figure 2) equipped with a magnetic stir bar were placed oligomer phosphite (0.5 g, 0.25 mmol $P(OPh)_2$), anhydrous $Ni(acac)_2$ (0.06 g, 0.24 mmol), and dry toluene (30 mL). The reaction apparatus was connected to an assembly of valves, charging port, pressure gauge, and a relief valve by a pressure coupling. The suspension was subjected to two freeze–pump–thaw cycles, then was heated to 95 °C to obtain a pale green solution. On cooling this solution, a pale green suspension was obtained. This suspension was cooled further to −20 °C and butadiene (3 g, 56 mmol) was introduced. With good stirring, a solution of $Al(Et)_3$ in hexane (0.8 mL, 0.8 mmol) was added via syringe to the cold suspension. The suspension first turned light brown and then amber as it warmed to room temperature. Heating to 95 °C produced a solution whose color ranged from dark yellow to amber depending on the ligand used. The reaction mixture was visually homogeneous. The reaction was complete in 5 h based on the observation that no further decrease in butadiene pressure was seen. At the end of the reaction, the solution was cooled to obtain a red-yellow suspension of the oligomeric catalyst. The supernatant was usually clear at this stage although the first cycle's supernatant in some runs had a light yellow color. The slurry of the precipitated catalyst along with the solvent and reaction products was transferred by forced siphon using argon pressure through a cannula into an argon-flushed centrifuge tube capped with a septum stopper. The suspension of the catalyst was centrifuged and the supernatant was removed by forced siphon under argon using a cannula. The precipitate containing the catalyst was washed twice with 25-mL portions of toluene and the washings were checked by GC for cyclooligomerization products. After two washings no products were detected. Dry toluene (30 mL) was added to the precipitated catalyst, and then the resulting slurry of catalyst was transferred back to the Lab Crest pressure bottle described above. The cyclooligomerization reaction was repeated using only a fresh charge of butadiene and heating the suspension to 95 °C for 5 h. The separation, recovery, and recycling of the catalyst was continued three times.

Determination of Nickel Leached from the Catalyst. Nickel in the product solution from the second cycle of a cyclooligomerization carried out in the presence of the oligomeric phosphite ligand **6a** was determined in the following way: A weighed sample of about 1–2 g of the supernatant from the second cycle of this cyclooligomerization was evaporated in a 20-mL porcelain crucible. Concentrated $\mathrm{H_2SO_4}$ (1 mL) was added to the residue and the crucible was gently heated on a hot plate for 2 h until the residue was completely decomposed. When 70% $\mathrm{HNO_3}$ (1 mL) was added dropwise followed by further heating on the hot plate for 15–20 h with occasional shaking of the contents. A clear pale yellow solution was obtained after the acid digestion was diluted with distilled water to 25 mL in a volumetric flask. The resulting solution was analyzed by ICP[24] and showed that the leachate contained 5 ppb of Ni, which corresponds to <0.01% of the nickel in the initial catalyst charge.

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Registry No. **7a**, 100781-90-6; **7b**, 105281-83-2; **7c**, 100781-89-3; **11b**, 105281-84-3; **11c**, 105281-85-4; COD, 111-78-4; VCH, 100-40-3; CDT, 676-22-2; 4-$\mathrm{MeOC_6H_4CH_2Cl}$, 824-94-2; 4-$\mathrm{MeOC_6H_4MgCl}$, 699-19-4; $\mathrm{I(CH_2)_9CH_3}$, 629-93-6; 4-$\mathrm{MeOC_6H_4(CH_2)_{18}CH_3}$, 105281-80-9; 4-$\mathrm{HOC_6H_4(CH_2)_{18}CH_3}$, 105281-81-0; 2-$\mathrm{PhC_6H_4OH}$, 90-43-7; (2-$\mathrm{PhC_6H_4O)_2PCl}$, 105281-82-1; $\mathrm{ClP(OEt)_2}$, 589-57-1; $\mathrm{ClP(OPh)_2}$, 5382-00-3; (2-$\mathrm{CH_2)_{17}CH_3}$, 26762-44-7; triphenyl phosphite, 101-02-0; tris(*o*-tolyl) phosphite, 2622-08-4; tris(*o*-biphenylyl) phosphite, 2752-19-4; ethylene, 74-85-1; butadiene, 106-99-0.

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Disproportionation of Quinone Radical Anions in Protic Solvents at High pH[1]

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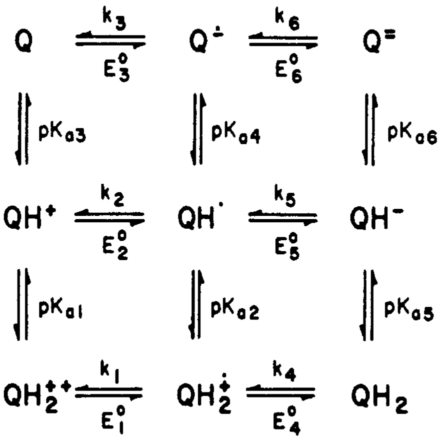
The voltammetry of anthraquinone, anthraquinone-2-sulfonate, and anthraquinone-2,6-disulfonate has been examined in aqueous and alcoholic solutions with tetraethylammonium hydroxide as the supporting electrolyte. At basic values of pH, the product of the two-electron reduction of each of these species is the dianion. The reduction process is found to proceed in two well-defined, one-electron steps in basic 2-propanol and ethanol. In basic methanol the two one-electron waves virtually overlap, and complete wave overlap is observed in basic aqueous solution. The differences in the half-wave potentials for the one-electron steps have been used to calculate the equilibrium constant for disproportionation of the radical anions in each solution. The logarithm of the equilibrium constant is found to correlate directly with the ability of the solvent to hydrogen bond, as determined by regression against Taft's scale of hydrogen-bond donor acidities. Thus, these data clearly show the strong influence of solvent–anion interactions on the thermodynamics of the reduction steps for anthraquinones.

Electron-transfer reactions that involve quinones, hydroquinones, and catechols are important in many areas of chemistry, especially in biological systems. Thus, it is not surprising that the thermodynamic parameters that govern these reactions have been studied extensively by pulse radiolysis[2] and electrochemical techniques.[3] Electron spin resonance has been used to demonstrate the presence of quinone radicals as intermediates in the redox processes of hydroquinones in aqueous solution.[4,5] The radical intermediates have been characterized with UV-visible spectroscopy following pulse radiolysis in aqueous solutions.[2,6-9] These measurements have been used to determine the acidity constants of radicals[10] and to provide an indirect measure of the standard reduction potentials ($E°$) for the one-electron processes.

Scheme I



The nine-member box scheme (Scheme I) summarizes the possible intermediates for all two-electron, two-proton

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