

Functionalized Ethylene Oligomers as Phase-Transfer Catalysts

David E. Bergbreiter* and J. R. Blanton

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received July 30, 1985

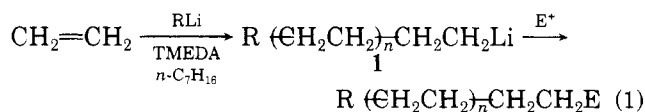
Ethylene oligomers with M_v in the range 1000-3000 containing terminal groups such as crown ethers, azacrown ethers, and phosphonium salts have been prepared and used as phase-transfer catalysts. These oligomeric catalysts have solubility properties similar to polyethylene in that they are insoluble at 25 °C but dissolve in organic solutions at elevated (90-110 °C) temperatures. Such oligomeric phase-transfer catalysts have activities comparable to their low molecular weight congeners and to activities reported for insoluble polystyrene-bound phase-transfer catalysts. After these oligomeric catalysts have been used in a reaction at 100 °C, they can be readily separated from the reaction products by cooling to form a precipitate, which can then be isolated by filtration. Such catalysts may be reused without loss of activity. These catalysts are also effective in "solid-liquid" phase-transfer reactions in which an inorganic solid is suspended in a hot organic solution containing catalyst and substrate.

Phase-transfer catalysis is typically carried out with catalysts that are soluble in organic solvents and that possess one or several sites which can bind a water-soluble salt either by coordination of the cation by a neutral ligand or by ion exchange.¹ Within the last ten years, insoluble polymeric ammonium salts, phosphonium salts, and crown ethers have been described which can substitute for the original low molecular weight species used as phase-transfer catalysts.²⁻⁴ Such polymeric species have an advantage of ready recyclability. A disadvantage of insoluble polymeric phase-transfer catalysts is that diffusion of reagents and substrates into and out of an insoluble polymer matrix can affect the catalyst's reactivity.^{3,5} While such diffusional restrictions can lead to novel selectivity due to size differences of otherwise similar organic substrates,⁶ this limitation on these catalysts' activity is more often a matter of concern either synthetically or in mechanism studies. Insoluble polymer-bound phase-transfer catalysts can also be used in "solid-solid" reactions where the inorganic material is not dissolved in water but is instead present as a suspension in an organic solvent. Phase-transfer catalysis has been noted under such solid-solid conditions but the way or ways in which an insoluble catalyst functions under such conditions is unclear. Here we describe alternative soluble, recyclable polymer-bound phase transfer catalysts derived from functionalized ethylene oligomers. These catalysts which we have prepared have the solubility characteristics of polyethylene. Namely, they are soluble in many organic solvents at 100 °C but are insoluble in the same solvents at 25 °C.⁷ We have found that this large temperature-dependent solubility difference can be used to recover and separate these oligomeric phase-transfer catalysts from the reaction products or starting materials of a given reaction by the simple expedient of cooling a hot solution of the functionalized ethylene oligomer and then separating the recovered solid oligomer by centrifugation or filtration. As is shown in the work described below, these terminally

functionalized ethylene oligomers act as phase-transfer catalysts under both "liquid-liquid" and "solid-liquid" conditions.

In the course of other work in our group directed toward development of new selective methods for functionalization of polymers,⁷ we have found that linear ethylene oligomers whose M_v is greater than 1200 have a useful temperature-dependent solubility. That is, such oligomers are insoluble in common organic solvents at 25 °C but do dissolve on heating. When a solution of these oligomers is cooled to room temperature, the oligomer reprecipitates as a fine powdery precipitate which can be separated from the solvent by centrifugation and decantation or by filtration. If a mixture of polyethylene and these oligomers is prepared and heated to effect dissolution in a solvent like toluene and the resulting solution is cooled, a coarser precipitate of polyethylene containing these oligomers forms which is readily isolated by filtration. We have recently described examples of chemistry in which such recovery procedures can be used with both polyethylene-bound reagents and transition-metal catalysts.⁸⁻¹⁰ This paper describes the extension of these methods to include nonmetallic phase-transfer catalysts.

Several methods can be used to prepare ethylene oligomers such that functional groups capable of forming or acting as phase-transfer catalysts are incorporated at a terminal position. Anionic oligomerization has proven to be the most useful of these methods.¹¹ In particular, anionic oligomerization of ethylene using *n*-butyllithium as an initiator (eq 1) is the most useful method for the preparation of terminally functionalized phase-transfer catalysts because the oligomers produced in this oligomerization reaction are strictly linear and can be recovered by precipitation with or without added polyethylene. By



using a range of different electrophiles (E^+), various end groups can be introduced at the terminus of the alkene oligomer. For example, ClPPh_2 or CO_2 followed by H^+ /

(1) Weber, W. P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Synthesis"; Springer-Verlag: Berlin, 1977. Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978.

(2) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147-200.

(3) Ford, W. T.; Tomoi, M. *Adv. Polym. Sci.* **1984**, *55*, 49-104.

(4) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421-429.

(5) Tomoi, M.; Yanai, N.; Shiiki, S.; Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 911-926.

(6) Regen, S. L.; Nigam, A. *J. Am. Chem. Soc.* **1978**, *100*, 7773-7775. Tomoi, M.; Ford, W. T. *Ibid.* **1981**, *103*, 3828-3832.

(7) Bergbreiter, D. E.; Chen, Z.; Hu, H.-P. *Macromolecules* **1984**, *17*, 2111-2116.

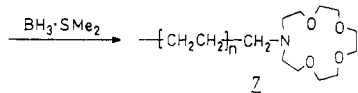
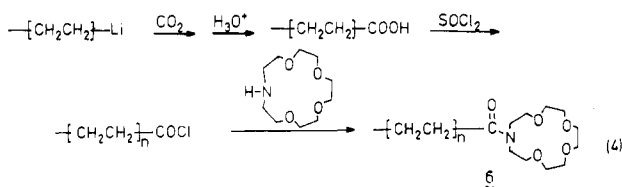
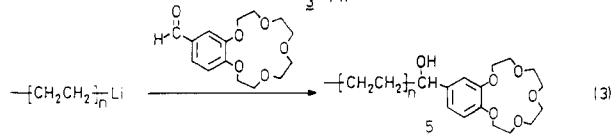
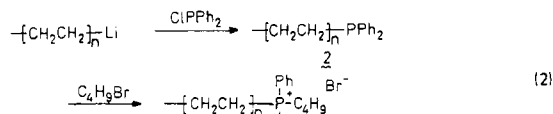
(8) Bergbreiter, D. E.; Blanton, J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 337-338.

(9) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1985**, *107*, 4792-4793.

(10) Bergbreiter, D. E.; Chandran, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1396-1397.

(11) Electrophilic substitution of living polymers derived from alkyl-lithium initiated oligomerization is discussed in: Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1-90.

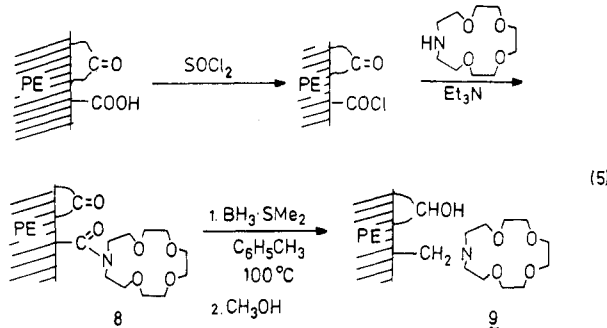
H₂O can be used to prepare a polyethylenediphenylphosphine or a carboxylated ethylene oligomer, respectively. The living oligomer 1 produced in eq 1 can thus be readily transformed either directly or indirectly into analogues of known phase-transfer catalysts (eq 2-4).



An advantage of procedures 2-4 over syntheses of divinylbenzene (DVB) cross-linked insoluble polystyrene-bound phase-transfer catalysts is that it is much easier to characterize the products of reactions 2-4. As is the case for insoluble polymer-bound catalysts, these oligomers can be characterized by IR as solids. Unlike insoluble polymer-bound catalysts, multinuclear NMR spectroscopy can also be used to both determine the identity of the attached functional groups and to determine the success of any given reaction. ¹H NMR spectroscopy is particularly useful. While the oligomers 1-7 all contain a large broadened peak due to the CH₂ groups, the methyl end and the functional group end of the oligomer both contain groups that are separated enough from the methylene envelope to be observed even at 90 MHz. Integration of the terminal groups' protons at higher fields or relative to an internal standard at 90 MHz directly yields quantitative data about the identities and loading of functional groups on these oligomers.¹² The results of such ¹H NMR studies yield molecular weight information and, more importantly, allow the success of the syntheses in eq 2-4 to be monitored and verified. ¹³C or ³¹P NMR spectroscopy can also be used with these to study these oligomers as well. While it is known that ¹³C and ³¹P NMR spectroscopy can be used to study functionalization of insoluble lightly DVB cross-linked polystyrene,¹³ the solubility of the oligomeric catalysts described in this work facilitates their analysis by ¹³C or ³¹P NMR spectroscopy.

While most of our work to date has involved use of terminally functionalized ethylene oligomers derived from anionic oligomerization of ethylene, we briefly examined the utility of more readily available and inexpensive

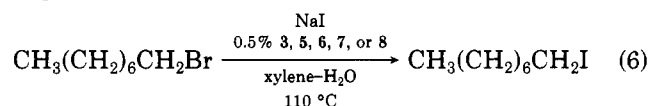
functionalized ethylene oligomers derived from oxidized polyethylene. Oxidized polyethylene is commercially available as a derivative of polyethylene and contains both carboxylic and ketone functionality.^{14,15} Although this polyfunctionality and the possibility of multiple functional groups per chain complicate any mechanistic studies and make characterization of the polymer derivative less feasible, we have found that it is possible to prepare phase-transfer catalysts using eq 5 (PE = polyethylene). Both



the polyethylenecarboxamide derivative 8 of aza-15-crown-5 and the corresponding amine 9 were prepared. While the carboxamide 8 was not a very active phase-transfer catalyst, the amine 9 had activity comparable to that of an aza-15-crown-5 or 15-crown-5 derivative of a linear ethylene oligomer.

As is shown by the results described in Tables I and II, the phase-transfer catalysts derived from eq 2-5 all are active as phase-transfer catalysts in nucleophilic substitution reactions and in reduction of carbonyl compounds with sodium borohydride under liquid-liquid conditions. In a typical procedure under liquid-liquid conditions, the oligomeric crown ether was dissolved in an organic solvent like xylene at 90-110 °C to form a 0.003 M solution. The organic substrate was then added such that the resulting solution was ca. 0.1 M in substrate. Excess inorganic substrate in water was added to give a two-phase mixture which was stirred magnetically. The use of a Vibromixer for agitating the reaction mixture was briefly examined but was not continued since no significant increase in reaction rate was noted.¹⁶ Kinetic data given in Table I were obtained by periodically removing aliquots from the organic phase and analyzing them by GC using hydrocarbon internal standards. The observed rates are such that half-lives of these reactions are in the range 1-8 h at convenient catalyst concentrations. These half-lives are comparable to those seen with other insoluble polymer-bound phase-transfer catalysts and are short enough to be synthetically practical.

In order to evaluate the activity of functionalized ethylene oligomers as phase-transfer catalysts and to compare them to known low molecular weight and insoluble polymer-bound phase-transfer catalysts, we have examined a series of reactions. In the case of phase-transfer catalysis under liquid-liquid conditions, we studied the nucleophilic substitution of iodide for bromide (eq 6). Numerous literature studies have measured the



(12) We have now further improved the procedure for ¹H NMR analysis of linear ethylene oligomers by using *tert*-butyllithium as the initiator in the oligomerization reaction 1. The methyl end of this *tert*-butyl group are better resolved from the methylene envelope of the ethylene oligomer and more readily analyzed by ¹H or ¹³C NMR spectroscopy. Bergbreiter, D. E.; Treadwell, D. T., unpublished results.

(13) Ford et al. (Ford, W. T.; Periyasamy, M.; Spivey, H. O. *Macromolecules* 1984, 17, 2881-2886 and references therein) describe some aspects of ¹³C NMR of functionalized DVB cross-linked polystyrenes. Examples of ³¹P NMR spectroscopy of functionalized DVB cross-linked polystyrene can be found in: Naaktgeboren, A. J.; Nolte, J. M. R.; Drenth, W. *J. Am. Chem. Soc.* 1980, 102, 3350-3354.

(14) Oxidized polyethylene containing 0.6 mequiv of CO₂H/g of polymer is available from Aldrich Chemical Co.

(15) Nuzzo, R. G.; Smolinsky, G. *Macromolecules* 1984, 17, 1013-1019.

(16) Balakrishnan and Ford (Balakrishnan, T.; Ford, W. T. *J. Org. Chem.* 1983, 48, 1029-1035) reported no advantage for use of a Vibromixer instead of use of magnetic or overhead stirrers.

Table I. Phase-Transfer Catalysis under Liquid-Liquid Conditions Using Functionalized Ethylene Oligomers as Recoverable Catalysts^a

catalyst ^b	substrate		product	10 ⁵ k _{obsd} , s ⁻¹ (mequiv of cat.) ⁻¹
	organic	inorganic		
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	83
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	8 ^c
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	KI	CH ₃ (CH ₂) ₆ CH ₂ I	83
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Cl	NaBr	CH ₃ (CH ₂) ₆ CH ₂ Br	42
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CHO	NaBH ₄	CH ₃ (CH ₂) ₆ CH ₂ OH	33
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	c-C ₆ H ₁₁ Br	NaI	c-C ₆ H ₁₁ I	<i>d</i>
C ₁₈ H ₃₇ P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	100
PS-(CH ₂) ₇ P(n-C ₄ H ₉) ₃ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	48 ^e
benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	72
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	KI	CH ₃ (CH ₂) ₆ CH ₂ I	0
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	28
				27 ^f
				35 ^g
PE-CO-aza-15-crown-5	CH ₃ (CH ₂) ₅ CH ₂ Br	NaI	CH ₃ (CH ₂) ₅ CH ₂ I	5
PS-CO-aza-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	43 ^h
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CHO	NaBH ₄	CH ₃ (CH ₂) ₆ CH ₂ OH	27
benzo-15-crown-5	CH ₃ (CH ₂) ₆ CHO	NaBH ₄	CH ₃ (CH ₂) ₆ CH ₂ OH	67

^a Reactions were run at 110 °C using 2 mM xylene solutions of the catalyst (*M_v* = 1300) and a 10-fold excess of the inorganic substrate dissolved in 5 mL of water. Agitation of the reaction mixtures was achieved with magnetic stirring. The reaction progress and the product identities were measured with GC or GC/MS. ^b PE stands for an oligomeric ethylene chain. PS stands for 2% DVB-crosslinked polystyrene. ^c The catalyst was heated at 135 °C for 3 h before being used. ^d <5% cyclohexyl iodide was formed in 70 h. ^e The literature data from ref 5. ^f *k*_{obsd} in second cycle using the oligomeric crown ether catalyst. ^g *k*_{obsd} in the fourth cycle using the oligomeric crown ether catalyst. ^h The literature data from: Montanari, F.; Tundo, P. *J. Org. Chem.* 1981, 46, 2125.

Table II. Phase-Transfer Catalysis under Solid-Liquid Conditions Using Terminally Functionalized Ethylene Oligomers as Recoverable Catalysts^a

catalyst ^b	substrate		product	10 ⁵ k _{obsd} , s ⁻¹ (mequiv of cat.) ⁻¹
	organic	inorganic		
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	92
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	8 ^b
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	LiI	CH ₃ (CH ₂) ₆ CH ₂ I	97
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	KI	CH ₃ (CH ₂) ₆ CH ₂ I	7
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	90 ^c
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₂ CH ₂ Br	NaI	CH ₃ (CH ₂) ₂ CH ₂ I	68
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	72
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₁₁ CH ₂ Br	NaI	CH ₃ (CH ₂) ₁₁ CH ₂ I	70
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Cl	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	8
PE-P(C ₆ H ₅) ₂ -n-C ₄ H ₉ ⁺	CH ₃ (CH ₂) ₆ CH ₂ Br	NaCN	CH ₃ (CH ₂) ₆ CH ₂ CN	83
benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	LiI	CH ₃ (CH ₂) ₆ CH ₂ I	27
benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	77
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	LiI	CH ₃ (CH ₂) ₆ CH ₂ I	12
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	43
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	KI	CH ₃ (CH ₂) ₆ CH ₂ I	0
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₂ CH ₂ Br	NaI	CH ₃ (CH ₂) ₂ CH ₂ I	27
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	27
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₁₁ CH ₂ Br	NaI	CH ₃ (CH ₂) ₁₁ CH ₂ I	33
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Cl	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	8
PE-benzo-15-crown-5	CH ₃ (CH ₂) ₆ CH ₂ Br	NaCN	CH ₃ (CH ₂) ₆ CH ₂ CN	23
PE-CO-aza-crown-5 ^d	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	2
PE-CH ₂ -aza-15-crown-5 ^d	CH ₃ (CH ₂) ₆ CH ₂ Br	NaI	CH ₃ (CH ₂) ₆ CH ₂ I	19

^a Reactions were run at 110 °C using 2 mM xylene solutions of the catalyst (*M_v* = 1300) and a 15-fold excess of the inorganic substrate. Agitation of the reaction mixtures was achieved with magnetic stirring. The reaction progress and the product identities were measured with GC or GC/MS. ^b The catalyst was heated to 135 °C for 3 h before being used. ^c The *M_v* of the catalyst was 1800. ^d The catalyst was derived from oxidized polyethylene according to eq 5.

rate of this reaction using a variety of catalysts. Thus, comparison of the catalysts we have prepared with other catalysts is simplified. In general, comparison of the rate constants obtained with functionalized ethylene oligomers as catalysts with data obtained by us for known low molecular weight phase-transfer catalysts or with the literature data for low molecular weight or divinylbenzene (DVB) cross-linked polystyrene-bound phase-transfer catalysts show our oligomeric catalysts are comparable in activity to other polymeric catalysts and slightly less active than a low molecular weight catalyst.

As can be seen from the data in Table I, ethylene oligomers containing crown ether groups have catalytic activity which is about one-third as great as the catalytic activity of nonpolymeric crown ethers. The activity as a

phase-transfer catalyst of a crown ether attached to the terminus of an ethylene oligomer is comparable to that of a similar crown ether attached to DVB cross-linked polystyrene as a phase-transfer catalyst. These oligomeric crown ethers can be recovered and reused through several reaction cycles. We were able to recover and recycle these catalysts through four reaction cycles without any appreciable loss in activity.

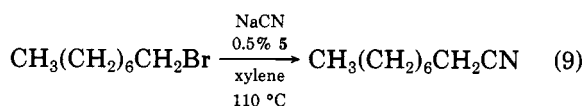
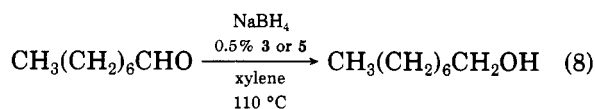
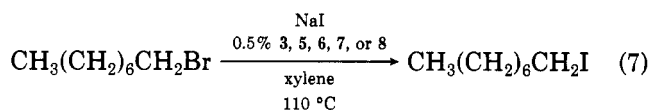
The polyethylenediphenylbutylphosphonium salts were found to be less stable than the oligomer-bound crown ether catalysts.³ Although they could be recycled with some loss of activity when used in successive reactions at 110 °C, heating these oligomeric phosphonium salts to 130 °C resulted in substantial loss of activity. NMR spectroscopic studies show that decomposition of **3** to poly-

ethylenediphenylphosphine oxide and alkenes occurs and is presumably the result of nucleophilic substitution and elimination reactions which occur with the alkylphosphonium salt or by attack of OH⁻ on the cationic phosphorus. Polyethylenediphenylphosphine oxide presumably forms by adventitious oxidation of polyethylenediphenylphosphine. Separate experiments showed that polyethylenediphenylphosphine oxide is not active as a phase-transfer catalyst.

Control experiments using polyethylene or oxidized polyethylene showed that no phase-transfer catalytic activity was seen with a polymer solution which did not contain a phase-transfer catalyst such as **3** or **5-9**. Control experiments also showed that an octadecylbutyldiphenylphosphonium bromide phase-transfer catalyst or benzo-15-crown-5 could not be used as recyclable phase-transfer catalysts in the presence of polyethylene. As expected, on the basis of our prior studies, a phase-transfer catalyst that is to be active and recyclable under our conditions has to contain both a suitable catalytic group and a polyethylene-like chain.⁸⁻¹¹

The size selectivity seen with insoluble polystyrene-bound phase-transfer catalysts is absent when these soluble oligomer-attached phase-transfer catalysts were used with various alkyl bromide substrates.⁶ Specifically, the rates of reaction of sodium iodide with *n*-butyl bromide, *n*-octyl bromide, or *n*-dodecyl bromide measured in the presence of a soluble oligomeric crown ether catalyst were identical within experimental error. This lack of sensitivity of reaction rate to substrate size is expected since mass transport of substrate through a porous polymer network to the catalyst center is kinetically unimportant when a soluble catalyst is used.

The solubility of these recoverable oligomeric phase-transfer catalysts also makes practical phase-transfer reactions under solid-liquid conditions (cf. Table II). Under these conditions, the inorganic substrate was simply suspended in an organic solvent, and the organic substrate and oligomeric phase-transfer catalyst were added. Heating dissolved the oligomeric catalyst which then catalyzed the reaction of interest. Pseudo-first-order rate constants measured in these solid-liquid reactions were generally comparable to those measured under liquid-liquid conditions. Workup of the reaction mixtures to recover the catalyst and isolate the organic products was generally easier under these solid-liquid conditions. In a typical workup procedure, the excess of inorganic reagents was first removed by hot filtration. Cooling the hot solution then precipitated the oligomeric catalyst. Filtration isolated the catalyst which could later be reused and yielded a colorless solution of the organic product. We consider these reactions to be more convenient to run than phase-transfer catalysis under liquid-liquid conditions. We tested the suitability of these catalysts in reactions 7-9.



In order to demonstrate the practicality of terminally functionalized ethylene oligomers as phase-transfer cata-

Table III. Solvent Effects on Polyethylene-*n*-butyldiphenylphosphonium Bromide Reaction of Sodium Iodide and 1-Bromooctane^a

solvent	10 ⁵ <i>k</i> _{obsd} , s ⁻¹ (mequiv of cat.) ⁻¹
<i>p</i> -xylene	83
octane	57
1,2,4-trichlorobenzene	55
1,1,2,2-tetrachloroethane	23
di- <i>n</i> -butyl ether	2

^aReactions were run at 110 °C using the liquid-liquid conditions described in the Experimental Section. Agitation of the reaction mixtures was achieved with magnetic stirring. The reaction progress was followed by GC.

lysts, we also carried out synthetic scale examples of reactions 6-8 under these solid-liquid conditions. Using 0.5% of **5** as a catalyst, we successively prepared 1-iodooctane, benzhydrol, and nonanenitrile according to eq 7-9 in 90%, 93%, and 85% isolated yields, respectively (see Experimental Section). These three successive preparative scale reactions were run on a 50-mmol scale, recovering and reusing the same sample of catalyst **5** in each successive reaction.

While these initial studies demonstrate the feasibility of these solid-liquid phase-transfer-catalyzed reactions they do not examine the relative kinetic importance of diffusion, trace water content, and intrinsic reactivity in reactions carried out under either liquid-liquid or solid-liquid conditions. We have made no effort as of yet to evaluate effects of particle size of the inorganic solid present in solid-liquid conditions. As noted in Table II, similar reactions using different catalyst preparations had measured rates which varied slightly. Nonetheless, from our preliminary experiments, significant differences in reactivity between different inorganic substrates can be seen. Using an oligomer-bound phosphonium salt as the catalyst, it was found that lithium iodide and sodium iodide were of comparable reactivity but that potassium iodide was much less reactive in nucleophilic substitution of 1-bromooctane. Similar results were obtained with the oligomer-bound crown ether. Nucleophilic substitution of 1-bromooctane occurred most readily in the latter case with sodium iodide. Lithium iodide reacted at a diminished rate, and no reaction was seen with potassium iodide in experiments using the same batch of oligomeric catalyst.

The size of the alkyl chain attached to a phase-transfer catalyst reportedly influences the activity of a catalyst, each additional methylene group in alkyl chains decreasing a catalyst's activity.¹⁷ In our experiments, we briefly examined the catalytic activity of ethylene oligomers containing phosphonium salts to see if there was a significant effect on their catalytic activity when the size of the oligomer chain was varied. While our results are complicated by the instability of the phosphonium salt, the observed catalytic activity ranged from 67 × 10⁻⁵ to 50 × 10⁻⁵ s⁻¹ (equiv of catalyst)⁻¹ in a series of reactions using oligomers whose *M*_v varied from 1300 to 1800 to 2500. Thus, ethylene oligomers whose *M*_v was 1300 tended to have slightly higher activity.

Solvent effects are seen in reactions of these oligomeric catalysts. As is the case with other low molecular weight catalysts, solvent effects appear to reflect changes in polarity and most likely reflect changes in intrinsic reactivity under conditions of differing polarity. Comparison of the pseudo-first-order rate constants measured with several

(17) Fieser, L. F.; Fieser, M. F. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 1158.

solvents of different polarity suggests that the reactions are most effective with lower polarity solvents (Table III).

In summary, oligomer-bound phase-transfer catalysts have activity comparable to that of both low molecular weight phase-transfer catalysts and to that of other insoluble polymer-bound phase-transfer catalysts. Such catalysts are available either by reaction of phosphines or crown ethers with commercially available polyethylene derivatives or from anionic oligomerization of ethylene. Very simple procedures permit ready separation of the catalyst from the reaction solution and catalyst recycling is practical. Oligomer-based catalysts merit attention as alternatives to both insoluble polymer-bound phase-transfer catalysts and conventional phase-transfer catalysts.

Experimental Section

General Methods. Carbon dioxide was purchased from Matheson Co. and ethylene was purchased from Air Products. All other chemicals and reagents used were obtained from Aldrich Chemical Co. When reactions employed reagents or formed products sensitive to either water or oxygen, solvents were purified by distillation from solutions or suspensions of sodium benzophenone ketyl under nitrogen prior to use. Tetramethylethylenediamine was purified to use by distillation from potassium metal and stored under nitrogen. Thionyl chloride was purified according to the literature method.¹⁷ 2,3-(4-Formylbenzo)-1,4,7,10,13-pentaoxocyclopentadecane (4) and 1-amino-4,7,10,13-tetraoxocyclopentadecane were prepared by minor modification of reported procedures.^{18,19} Magnetic stirrers were used to agitate reactions except as noted. Unexceptional experimental methods for handling organometallic reagents were used when water- and air-sensitive organometallic reagents were employed.²⁰ Gas chromatographic analyses were performed with a Hewlett-Packard Model 5830A GC. GC/MS analyses were performed with a Hewlett-Packard Model 5790A GC equipped with a Model 5970A mass selective detector. IR spectra were obtained with a Pye Unicam SP3-200 spectrometer. Band positions are reported in wave numbers. ¹H NMR spectra were obtained with Varian Model EM-390 or XL-200 spectrometers. NMR spectra of oligomers were obtained at elevated temperatures in toluene-*d*₆. ¹³C and ³¹P NMR spectra were obtained with a Varian Model XL-200 or FT-80 spectrometer. Peak positions in ¹H and ¹³C NMR spectra were measured relative to Me₄Si. Peak positions in ³¹P NMR spectroscopy are reported relative to an external solution of H₃PO₄.

Preparation of Lithiated Ethylene Oligomer. A dry 500-mL Fisher-Porter pressure bottle equipped with a magnetic stirring bar was connected to a multiple-use (vacuum, nitrogen, and ethylene) pressure line through a pressure coupling. This bottle was then evacuated and purged with nitrogen 3 times. Dry heptane (250 mL), 6 mL of 1.6 N *n*-butyllithium in hexane (10 mmol), and 4.4 mL of *N,N,N',N'*-tetramethylethylenediamine (ca. 30 mmol) were added successively by syringe. The bottle was pressurized with ethylene to 30 psi, and the oligomerization was carried out at this pressure for 48 h. During the oligomerization, a white precipitate of lithiated polyethylene 1 formed. This living oligomer was not itself characterized but rather was converted by electrophilic substitution reactions to the desired terminally functionalized ethylene oligomers described below. The measured *M_n* for different oligomerizations varied in successive preparations as can be deduced from the analytical data for the oligomers described below.

Preparation of Carboxylated Linear Ethylene Oligomer. The suspension of 1 prepared by the above procedure was cooled to -78 °C, any unreacted ethylene was removed at reduced pressure, and the bottle was filled with carbon dioxide to a

pressure of 30 psi. After 25 min of stirring under 30 psi of carbon dioxide at -78 °C, the supply of carbon dioxide was turned off, and the reaction mixture was allowed to warm to room temperature and stirred an additional 24 h. The resulting oligomer which now had a terminal lithium carboxylate group was isolated by filtration, washed with 400 mL of toluene, 400 mL of 95% aqueous ethanol, and 400 mL of methanol, and finally dried under reduced pressure at room temperature for 24 h. The oligomer was then separated from any insoluble salts by extraction with hot toluene in a Soxhlet apparatus for 24 h. Cooling the hot toluene solution of carboxylated oligomer produced during this extraction resulted in formation of a fine white powder, which was isolated by filtration, washed first with 400 mL of toluene and then with 100 mL of ether, and dried for 24 h at 25 °C in vacuo. IR analysis of this oligomer showed a characteristic band at 1575 cm⁻¹ due to the lithium carboxylate. Variations of this procedure sometimes led to formation of some undesired ketone byproduct whose presence was evidenced at this point by the appearance of a carbonyl stretch at 1710 cm⁻¹. Ketone formation was minimized by performing the carboxylation at low temperature as described above.²¹ Protonation of this lithium carboxylate was accomplished by refluxing 400 mL of a toluene solution of this oligomer with 4 mL of concentrated HCl for 24 h. The powdery carboxylic acid terminated ethylene oligomer was isolated from the hot toluene solution by cooling to form a precipitate. This precipitate was washed with 300 mL of toluene, 300 mL of a 50/50 (v/v) methanol/water mixture, and 200 mL of methanol and finally dried in vacuo for 48 h at 25 °C: IR (KBr disc) 2920, 2850, 1710, 1700, 1465, 730, 720 cm⁻¹. A total of 12 g of product oligomer was isolated by precipitation. Viscosimetric analysis showed that the linear ethylene oligomer derived from this reaction had an *M_n* of 2500. This product oligomer was insoluble in toluene at room temperature.²²

Preparation of Polyethylenediphenylphosphine (2). To a suspension of 30 mmol of 1 was added 10.6 mL (13.3 g, 60 mmol) of chlorodiphenylphosphine at 25 °C. After 1 h of stirring, the mixture was heated to 90 °C and vigorously stirred for an additional 12 h. Cooling precipitated the crude product phosphine, which was placed in a Soxhlet apparatus and extracted into a hot toluene solution. Cooling the hot toluene solution produced a crude phosphine product free of any insoluble salts but which invariably contained 10–30% polyethylenediphenylphosphine oxide on the basis of ³¹P NMR spectroscopy. This polyethylenediphenylphosphine oxide was suspended in toluene and allowed to react with 19.5 g (145 mmol) of trichlorosilane for 24 h at 25 °C. The bulk of the excess trichlorosilane was removed at reduced pressure. After the solid oligomer was isolated by filtration, it was suspended in 150 mL of 1 N KOH in isopropyl alcohol and stirred for 24 h. Filtration and washing of the solid product repeatedly with ethanol-water and then ethanol until the washings were no longer basic led to the product, which was dried in vacuo to yield 18 g of a white solid: IR (KBr pellet) 1180, 1120 cm⁻¹; ¹H NMR (toluene-*d*₆) δ 7.25 (br), 2.1 (m), 1.0–1.8 (br s), 0.9 (t, CH₃); ³¹P NMR (toluene) δ -16.6. The ³¹P NMR spectrum of 2 after reduction with trichlorosilane did not contain a peak at δ 27.3 due to polyethylenediphenylphosphine oxide. Integration of the aryl signals in the ¹H NMR vs. the signals of an internal standard, hexamethyldisiloxane, showed the oligomer contained 0.8 mequiv of PPh₂/g of oligomer.

Preparation of Polyethylenediphenyl-*n*-butylphosphonium Bromide (3). Polyethylenediphenylphosphine (5 g, 4 mequiv of PPh₂) was added to a 100-mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. After addition of 40 mL of toluene and 20 mL of *n*-butyl bromide, the mixture was heated to reflux under nitrogen. The resulting solution was stirred 36 h at reflux. Cooling this product solution to 25 °C precipitated the product oligomer, which was then isolated by filtration. After the crude product 3 was washed with ether to remove *n*-butyl bromide, the product phosphonium salt

(18) Ungaru, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* 1976, 98, 5198–5202.

(19) Maeda, H.; Furuyoshi, S.; Nakatusuji, Y.; Okahara, M. *Bull. Chem. Soc. Jpn.* 1983, 56, 212–218.

(20) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; Chapter 9.

(21) Hu, H.-P. Ph.D. Dissertation, Texas A&M University, August 1985.

(22) The *M_n* of the oligomers used in this work was determined at 80 °C in xylene by using a Mark-Houwink relationship with constants $\alpha = 0.63$ and $K = 1.35 \times 10^{-4}$ obtained from: Harris, I. *J. Polym. Sci.* 1952, 8, 353–364.

was dried 12 h in vacuo to yield 5.3 g of product: IR (KBr pellet) 1080 cm^{-1} (broad); ^1H NMR (toluene- d_6) δ 7.75 (br, s), 2.1 (m), 1.0–1.8 (a large br s), 0.9 (t, CH_3); ^{31}P NMR (toluene) δ 26. Integration of the aromatic signal vs. the signal of a known amount of an internal standard, hexamethyldisiloxane, indicated that the oligomer contained 0.7 mequiv of phosphonium salt/g of oligomer.

Preparation of Oligomer-Bound Benzo-15-crown-5 5. A suspension of 1 was prepared on a 3-mmol scale as previously described except that *n*-butyl ether was used as the solvent. To the resulting heterogeneous suspension of lithiated oligomer at 25 °C was added 0.96 g (3.2 mmoles) of 4 dissolved in hot *n*-butyl ether. The mixture was stirred at room temperature for 1 h and heated to 90 °C for 12 h. The product was isolated upon cooling by filtration. This resulted in the preparation of 1.5 g of product after purification from toluene: IR (KBr) 1170, 1120, 1080 cm^{-1} ; ^1H NMR (toluene- d_6) δ 3.6 (br s); ^{13}C NMR (toluene- d_6) δ 71.9, 71.8, 71.6, 71.5, 70.4, 70.3, 70.1, 32.4, 30.4, 30.2, 20.4, 14.1. Quantitative analysis of the signal at δ 3.6 relative to the singlet of an internal standard, hexamethyldisiloxane, showed that the loading of crown ether on the oligomer was 0.15 mequiv of crown/g of oligomer.

Preparation of Oligomer-Bound Monocarboxamido-15-crown-5 6. A 500-mL round-bottomed flask equipped with a stirring bar and reflux condenser was charged with 3.0 g (0.5 mequiv of $\text{CO}_2\text{H/g}$ of polymer) of an oligomeric carboxylic acid prepared as described above, 1 mL (excess) of SOCl_2 , 4 drops of dimethylformamide, and 150 mL of toluene. The mixture was heated to 100 °C to form a homogeneous solution. The oligomeric acid chloride formed was isolated as a crude solid by removal of solvent under reduced pressure and used directly in the next step after IR analysis showed the 1700- cm^{-1} peak had disappeared and a peak at 1780 cm^{-1} had appeared. Addition of 150 mL of toluene and 0.64 g (2.9 mmol) of monoaza-15-crown-5 to this crude acid chloride and heating at 100 °C for 12 h produced a solution of the product, which was isolated as a precipitate by cooling this hot solution. Filtration yielded 3.1 g of product in the form of a dark brown solid: IR (KBr) 1650 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (toluene- d_6) δ 3.5 (br s), 1.5 (br s), 0.9 (a virtually coupled triplet). In some preparations of the oligomeric carboxylic acid, a peak at 1710 cm^{-1} remained after carboxamide formation. This peak was evidently due to formation of some ketone during the carboxylation of the lithiated oligomer. Quantitative analysis of the signal at δ 3.5 relative to the singlet due to an internal standard, hexamethyldisiloxane, showed that the loading of monocarboxamido-15-crown-5 was 0.4 mequiv of crown/g of polymer.

Preparation of Polyethylene-Bound Carboxamido-15-crown-5 8. The procedure used for 6 was followed using polyethylene carboxylic acid chloride derived from oxidized polyethylene¹⁴ in accordance to the literature procedure.²³ The product 8 had absorptions at 1710 and 1650 cm^{-1} in the IR and a broad peak at δ 3.55 by ^1H NMR spectroscopy. Integration using an internal standard showed 0.45 mequiv of carboxamidocrown/g of polymer.

Preparation of Oligomer-Bound Monoaza-15-crown-5 7. A dry 200-mL round-bottomed flask was equipped with a magnetic stirring bar and reflux condenser. To this apparatus was added 1.1 g of 6 and 50 mL of toluene. The reaction vessel was then purged thoroughly with nitrogen, and 5 mL (10.1 M, 50.5 mmol) of neat borane–dimethyl sulfide was added using a syringe. The resulting mixture was heated to 110 °C by means of an oil bath. The solution that formed was stirred for 4 h at this temperature. At this point the apparatus was removed from the oil bath and cooled to room temperature under nitrogen. Once the reaction mixture had cooled, a second 5-mL portion of borane–dimethyl sulfide was added, and the reaction mixture was once again heated to 110 °C to form a clear solution that was allowed to stir overnight. The next day the product oligomer was obtained by cooling the reaction mixture to form a precipitate which was collected

by filtration. The collected solid was washed several times with acetone, a 50/50 (v/v) methanol/water mixture, and finally two 100-mL portions of petroleum ether. After drying under vacuum, the final oligomer product consisted of 1 g of a white solid whose IR spectrum no longer contained peaks at 1710 and 1650 cm^{-1} .

Preparation of Polyethylene-Bound Aza-15-crown-5 9. The carboxamide 8 was reduced with a hot toluene solution of borane–dimethyl sulfide to yield a product that had no carbonyl absorption in the IR by using the procedure described above for the reduction of 6 to 7. The product 9 had a broad multiplet at δ 3.5 in its ^1H NMR spectrum and contained 0.4 mequiv of crown ether/g of polymer on the basis of integration of this peak vs. a hexamethyldisiloxane internal standard.

General Procedure for Preparative Scale Phase-Transfer Reactions Using 5 as a Catalyst. To a 500-mL flask equipped with a magnetic stirring bar and reflux condenser were added 9.7 g (50 mmol) of 1-bromooctane, 2.0 g (0.3 mequiv) of 5, 25 g of sodium iodide, and 250 mL of toluene. The resulting heterogeneous mixture was heated to 110 °C with an oil bath and stirred vigorously for 16 h. Cooling the reaction mixture led to precipitation of 5. The precipitated 5 was separated by filtration to yield a colorless toluene solution of the product. The catalyst 5 was recovered from this mixture of catalyst, sodium iodide, and sodium bromide by washing first with water and then with acetone. The toluene was removed from the product under reduced pressure by using a rotary evaporator, and the pale yellow product so obtained was further purified by short-path distillation to yield 10.8 g (90% yield) of 1-iodooctane: bp 68–69 °C (1 torr) [lit. bp²⁴ 225 °C]; ^1H NMR (CDCl_3) δ 0.9 (t, 3 H), 1.3 (m, 10 H), 1.8 (t, 2 H), 3.2 (t, 2 H); ^{13}C NMR (CDCl_3) δ (CH_2), 33.6, 31.7, 30.5, 29.0, 28.4, 22.6 (CH_3) 14.0, (CH_2I) 7.0.

Benzhydrol was obtained in 93% yield from benzophenone by using the procedure described above for sodium iodide with the exception that 5 mL of water was also added to the reaction mixture. The product alcohol had mp 66–67 °C (lit. mp²⁵ 65.5–66.5 °C): ^1H NMR (CDCl_3) δ 2.2 (s, 1 H), 5.7 (s, 1 H), 7.3 (m, 10 H); ^{13}C NMR (CDCl_3) δ 142.7, 128.3, 127.5, 126.5, 76.0.

Nonanenitrile was prepared on a 50-mmol scale from 1-bromooctane in 85% yield following the same procedure described for preparation of 1-iodooctane. The product nonanenitrile was purified by distillation and had bp 63–64 °C (0.5 torr) [lit. bp²⁶ 140 °C (10 torr)]: ^1H NMR (CDCl_3) δ 0.9 (t, 3 H), 1.3–1.9 (m, 12 H), 2.4 (t, 3 H); ^{13}C NMR (CDCl_3) δ 13.8 (CH_3), 16.9, 22.4, 25.2, 28.5, 31.5 (CH_2), 119.5 (CN).

General Procedure for Kinetic Scale Reactions. Reactions were carried out in 50-mL round-bottomed flasks equipped with a septum-capped side arm, magnetic stirring bar and a reflux condenser. The flask was then charged with 25 mL of *p*-xylene, 0.07–0.1 mequiv of catalyst, 0.5–0.7 mmol of a straight chain hydrocarbon internal reference, and at least a 10-fold excess of the inorganic reagent (NaI , NaBH_4 , or NaCN) either as a solid or as a saturated aqueous solution. The resulting heterogeneous mixture was heated to 110 °C with an oil bath. After the oligomeric catalyst dissolved, 1.5–2.0 mmol of organic substrate was added as a xylene solution. The course of the reaction was monitored by gas chromatography by periodic removal of 1-mL aliquots which were treated with 1 mL of petroleum ether or hexanes to precipitate the oligomer before GC analysis. At the end of the reaction, the catalyst was separated from the solution of product by cooling to precipitate the catalyst. Filtration yielded a clear colorless solution of product.

Acknowledgment. Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, and to the Texas A&M Center for Energy and Mineral Resources for funding of this research.

(23) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1977, 99, 4746–4756.

(24) Cainelli, G.; Mannescalchi, F. *Synthesis* 1976, 472–473.

(25) Santaniello, E.; Ponti, F.; Mannocchi, A. *Synthesis* 1978, 891–892.

(26) Starks, C. M. *J. Am. Chem. Soc.* 1972, 93, 195–199.