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New Catalytic Systems for the Fixation of Carbon Dioxide. 1. Copolymerization of CO_2 and Propylene Oxide with New Rare-Earth Catalysts—$RE(P_{204})_3$–$Al(i\text{-}Bu)_3$–$R(OH)_n$

Xianhai Chen, Zhiquan Shen,* and Yifeng Zhang

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China

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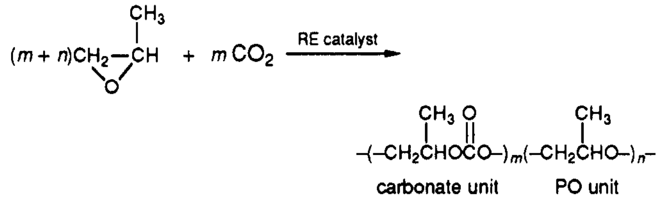
ABSTRACT: Copolymerization of propylene oxide and carbon dioxide was successfully carried out by using new rare-earth catalytic systems for the first time. It has been found that ternary rare-earth coordination catalysts composed of rare-earth phosphonate, triisobutylaluminum, and glycerine are effective catalysts for the copolymerization. The system $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine shows the highest activity. The yield and intrinsic viscosity of the copolymer depend significantly on the molar ratio of catalyst components and the reaction condition. The copolymers prepared were characterized by IR, ^1H NMR, GPC, and DTA–TGA. It is showed that the copolymers obtained have a high molecular weight with a narrow molecular weight distribution and a high thermal stability. The carbonate unit content of the methanol-insoluble copolymer is as high as 30–40%.

Chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. As a kind of catalytic fixation of carbon dioxide, copolymerization reactions of carbon dioxide with various epoxides have been investigated extensively in recent years. The effective catalysts reported so far for the copolymerization consist of diethylzinc and compounds with active hydrogen, such as water,[1] primary amine,[2] di- or trihydric phenol,[3] dicarboxylic acid,[4] polymer,[5], etc. However, the yield and molecular weight of the copolymer are still to be improved.

Recently, we have found that rare-earth coordination catalysts are very effective catalysts for the ring-opening polymerization or copolymerization of alkylene oxide and sulfide, such as ethylene oxide,[6] propylene oxide,[7] epichlorohydrin,[8] and propylene sulfide,[9] giving high molecular weight polymers with a high rate. In this paper, the exploitation of new catalysts composed of rare-earth compounds for the copolymerization of carbon dioxide with propylene oxide (PO) has been reported for the first time. The catalytic systems, especially $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine, give a high yield within a short time. Also, the copolymers obtained are random copolymers with a high molecular weight, a narrow molecular weight distribution, and a high thermal stability:



$$(m+n)CH_2\text{–}CH(CH_3)\text{(–O–)} + m\,CO_2 \xrightarrow{\text{RE catalyst}} \text{–}(\text{–}CH_2CH(CH_3)OC(=O)O\text{–})_m(\text{–}CH_2CH(CH_3)O\text{–})_n\text{–}$$

Experimental Section

Materials. Propylene oxide, 1,4-dioxane, toluene, and other solvents were purified by the usual methods before use. Commercial carbon dioxide (purity more than 99.9%) was used without further purification. Rare-earth complexes $RE(P_{204})_3$ (RE = La, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y; P_{204} = $(RO)_2P(O)O$–, R = $CH_3(CH_2)_3CH(C_2H_5)CH_2$–) were prepared by using the method described in ref 10. A toluene solution of $RE(P_{204})_3$–$Al(i\text{-}Bu)_3$ was prepared according to ref 6. The catalysts $RE(P_{204})_3$–$Al(i\text{-}Bu)_3$–III were obtained under a nitrogen atmosphere by dropwise addition a 1,4-dioxane solution of the third component (III) into the solution of $RE(P_{204})_3$–$Al(i\text{-}Bu)_3$.

Copolymerization. Copolymerization of carbon dioxide with PO was carried out in a 80-mL stainless steel autoclave. After the reaction was completed, the reaction mixture was terminated with methanol containing 5% hydrochloric acid. The resulting copolymer was precipitated by water, washed with water several times, and then dried in vacuo at room temperature.

Analysis of Copolymer. The ^1H NMR spectra of the copolymer in deuteriochloroform were measured at room temperature with a JEOL FX-90Q NMR spectrometer using tetramethylsilane (TMS) as the internal reference. The carbonate unit content of the copolymer (CU %) was calculated from the area ratio of peaks at 5.0, 4.2, and 3.5 ppm in the ^1H NMR spectrum according to the following equation:

$$\text{CU }\% = \frac{A_{5.0} + A_{4.2}}{A_{5.0} + A_{4.2} + A_{3.5}}$$

IR spectra of the copolymer films were recorded on a Nicolet 5D FTIR spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 208 LC/GPC equipped with a differential refractometer detector by using polystyrene (MW = 2350–1.2 × 10^6) as the standard. The thermal property of the copolymer was measured with a DT-30 calorimeter. The intrinsic viscosity of the copolymer was measured in benzene at 35 °C by using an Ubbelohde viscometer. The number-average molecular weight of the copolymer was calculated according to the following equation:[11]

$$[\eta]\ (\text{dL/g}) = 1.11 \times 10^{-4} \bar{M}_n^{\,0.8}$$

Results and Discussion

Copolymerization of CO_2 and PO with Various Rare-Earth Systems. Combinations of 14 rare-earth phosphonates, $RE(P_{204})_3$, with $Al(i\text{-}Bu)_3$ and glycerine were used as catalysts for the copolymerization of carbon dioxide and PO. The results are summarized in Table I. It has been found that all these rare-earth coordination catalysts are effective catalysts for the fixation of CO_2, but the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine system is the most outstanding catalyst among the combinations tested, because it gives both a high yield and a high molecular weight copolymer. So the studies were focused on the Y catalyst systems. The reason for yttrium and lutetium systems showing a higher activity probably is that their electronic structures are more appropriate for the active species formation.

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Table I
Copolymerization of PO and CO_2 with $Re(P_{204})_3$–$Al(i\text{-}Bu)_3$–Glycerine[a]

RE	yield, g/mol of Y	[η], dL/g	$\bar{M}_n \times 10^{-4}$
Sc	1223	0.315	2.07
Y	1672	3.82	46.9
La	697	0.485	3.55
Nd	973	0.417	2.94
Eu	855	1.04	9.22
Gd	552	0.210	1.25
Tb	894	0.093	0.45
Dy	934	1.00	8.78
Ho	1289	0.545	4.12
Er	473	0.330	2.20
Tm	158	0.690	5.52
Yb	1210	0.600	6.63
Lu	1525	1.67	16.7

[a] Al/RE = 8; III/Al = 0.5; (PO) = 2.15 mol/L; 30–40 atm of CO_2; 17 h; 60 °C; (RE) = 0.038 mol/L; 1,4-dioxane + toluene (4:1) as solvent.

Table II
Effect of the Structure of Component III on Catalytic Activity[a]

no.	III	yield	[η], dL/g	$\bar{M}_n \times 10^{-4}$
1	H_2O	1052	1.58	15.5
2	CH_3OH	295	1.19	10.9
3	$HOCH_2CH_2OH$	715	0.73	5.9
4	glycerine	2451	3.87	47.6
5	2-propanol	421	0.69	5.5
6	n-C_4H_9OH	515	1.02	9.0
7	$(CH_3)_3COH$	663	1.13	10.2
8	propylene glycol	263	0.89	7.6
9	2-butyne-1,4-diol	842	2.03	21.3
10	CH_3OH/glycerine (1:1)	552	2.01	21.0
11	glycerine/CH_3OH (1:1)	842	2.54	28.1
12	CH_3OH/glycerine/CH_3OH (1:2:1)	1197	3.44	41.1

[a] Al/Y = 8; III/Al = 0.5; (PO) = 2.15 mol/L; 30–40 atm of CO_2; 60 °C; 16 h; dioxane. Nos. 1–8: (Y) = 4.76 × 10^{-2} mol/L. Nos. 9–12: (Y) = 3.8 × 10^{-2} mol/L.

Effect of the Structure of Component III on Catalytic Activity. It has been found that the catalytic activity appeared to be strongly dependent on the nature of the third component of the rare-earth catalyst. Table II illustrates the results of the effect of various III components on the copolymerization of PO and carbon dioxide with the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$ system. All of the catalyst systems tested seemed to be active for the copolymerization of PO and carbon dioxide. The products obtained are random copolymers, with a carbonate unit content from 10% to 30% having a structure of polycarbonate with some ether linkage (characterized by IR and ^1H NMR). It was noteworthy that the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine system showed the highest activity in the copolymerization reaction, giving a high yield as well as a high molecular weight copolymer. It is reasonable to assume that glycerine might incorporate into the active species, as in the case of the zinc system.[12]

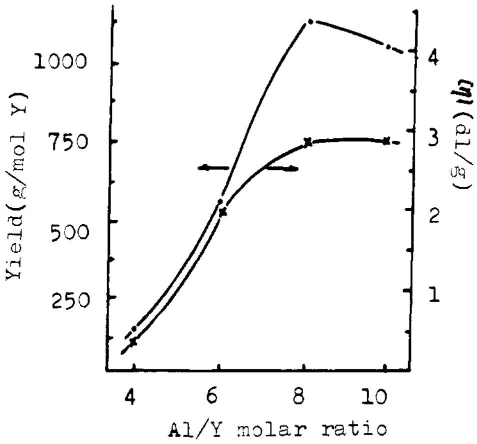

Figure 1. Effect of Al/Y molar ratio on copolymerization. Conditions: III/Al = 0.5; [Y] = 4.76 × 10^{-2} mol/L; [PO] = 2.15 mol/L; 30–40 atm of CO_2; 60 °C; 10 h; 1,4-dioxane + toluene (4:1) as solvent.

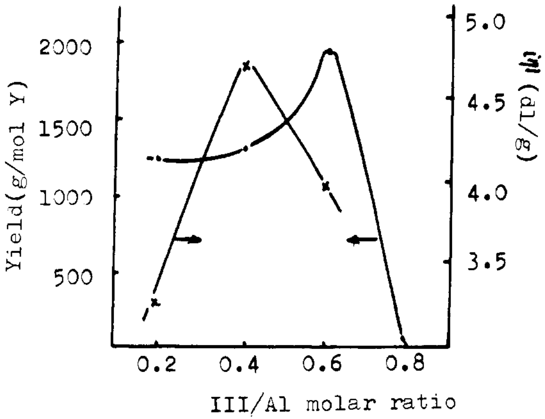

Figure 2. Effect of glycerine/Al molar ratio on the copolymerization. Conditions: Al/Y = 8; [Y] = 4.76 × 10^{-2} mol/L; [PO] = 2.15 mol/L; 30–40 atm of CO_2; 60 °C; 16 h; 1,4-dioxane + toluene (4:1) as solvent.

Characteristics of the Copolymerization with $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–Glycerine. The catalyst component ratios of the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine system are the most important factors influencing the copolymerization of PO and carbon dioxide. Figures 1, 2 present the dependence of the copolymer yield and intrinsic viscosity on the molar ratio of the catalyst components, i.e., Al/Y and glycerine/Al molar ratios. It is seen from Figure 1 that the copolymer yield and intrinsic viscosity both increase with an increase of the Al/Y molar ratio, and the intrinsic viscosity of the copolymer attains a maximum value. The optimum Al/Y molar ratio for the copolymerization is 8. It seems that a kind of bimetallic species formed at Al/Y = 8 involving Al and Y is responsible for the high yield and high molecular weight of the copolymer. Figure 2 indicates that both the copolymer yield and the intrinsic viscosity have maximum values at 0.6 and 0.4 glycerine/Al molar ratios, respectively. The highest intrinsic viscosity reaches 4.73 dL/g ($\bar{M}_n$ = 61 × 10^4). It seems that an excess amount of glycerine might destroy the bimetallic catalyst species, thus decreasing the yield and [η].

Figure 3 shows the effect of catalyst concentration on the copolymerization, retaining other conditions: [PO] = 2.15 mol/L, Al/Y = 8, III/Al = 0.5, 30–40 atm CO_2, 60 °C, 18 h. It has been found that the yield and intrinsic viscosity of the copolymer increase rapidly with an increase of the catalyst concentration when [Y] is from 2.6 × 10^{-2} to 3.9 × 10^{-2} mol/L. The most favorable catalyst concentration is in the range of 3.8 × 10^{-2}–5.7 × 10^{-2} mol/L.

The $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine system exhibited a pattern of the reaction time dependence of the copolymer yield and molecular weight similar to that of other systems reported.[13] During the reaction, both the yield and the molecular weight of the copolymer increased with an increase of the reaction time to a maximum (Figure 4). This agrees with an anionic coordinate polymerization mechanism.[13] A little drop of the intrinsic viscosity of the copolymer at more than 40 h was probably due to the copolymer degradation in the presence of catalyst as reported by Kuran.[14]

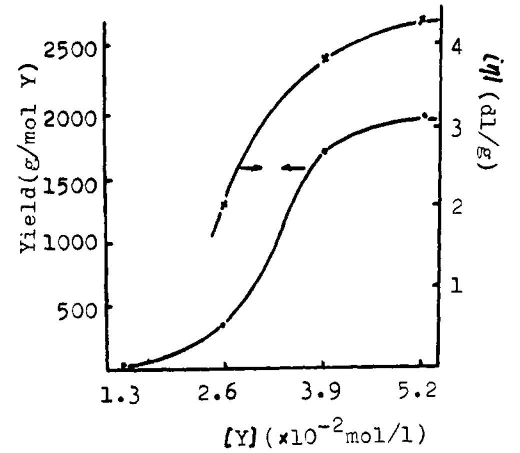

Figure 3. Effect of catalyst concentration on the copolymerization. Conditions: Al/Y = 8; glycerine/Al = 0.5; [PO] = 2.15 mol/L; 30–40 atm of CO_2; 60 °C; 18 h; 1,4-dioxane + toluene (4:1) as solvent.

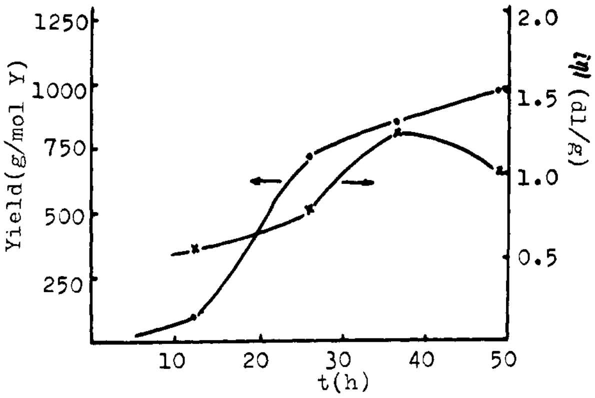

Figure 4. Reaction time dependence of the copolymer yield and the intrinsic viscosity. Conditions: 20 °C; [PO] = 2.15 mol/L; 30–40 atm of CO_2; [Y] = 3.8 × 10^{-2} mol/L; Al/Y = 8; III/Al = 0.5; 1,4-dioxane + toluene (4:1) as solvent.

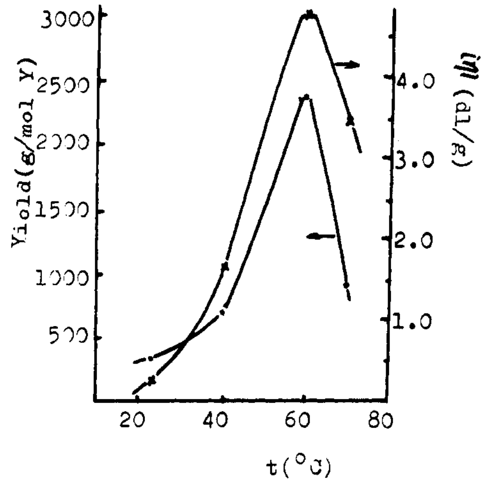

Figure 5. Influence of reaction temperature on the yield and [η] of copolymer. Conditions: Al/Y = 8; III/Al = 0.5; [Y] = 3.8 × 10^{-2} mol/L; 24 h; 30–40 atm of CO_2; [PO] = 2.15 mol/L; 1,4-dioxane + toluene (4:1) as solvent.

The effect of reaction temperature on the copolymerization is illustrated in Figure 5. Both the yield and the intrinsic viscosity of the copolymer have maximum values at 60 °C. The decrease of the yield and the intrinsic viscosity of the copolymer at more than 60 °C may be caused by the depolymerization and degradation of the copolymer.[13]

Table III
Copolymerization of PO with CO_2 in Different Solvents by Using $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–Glycerine as Catalyst[a]

no.	solvent	yield, g/mol of Y	[η], dL/g
1	benzene	1420	2.95
2	THF	302	0.37
3	ether	329	0.88
4	2-butanone	no polymer	
5	DMF	no polymer	
6	cyclohexane	1986	2.75
7	petroleum benzin	1670	2.75
8	toluene	3064	1.07
9	CH_2Cl_2	trace	
10	1,4-dioxane/benzene (1:1)	3274	0.94

[a] Al/Y = 8; III/Al = 0.5; (Y) = 3.8 × 10^{-2} mol/L; (PO) = 2.15 mol/L; 17 h; 60 °C; 30–40 atm of CO_2.

Table IV
Some Properties of Three Specimens with Different Intrinsic Viscosities

	percentage,	[η],	CU	GPC[b] data		
sample[a]	%	dL/g	%	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	MWD
1		3.82		39.6	85.2	2.15
1 (S)	57			28.9	72.8	2.52
1 (I)	43		33	70.6	112.4	1.59
2		4.28		43.9	86.2	1.96
2 (S)	54			21.8	68.3	3.13
2 (I)	46		30	77.3	118.4	1.53
3		4.82		79.6	116.3	1.46
3 (S)	28			62.0	109.8	1.77
3 (I)	72		ca. 30	79.9	122.9	1.54

[a] S, methanol-soluble; I, methanol-insoluble. [b] All of the GPC curves have only one peak; measured at 30 °C; THF as eluent.

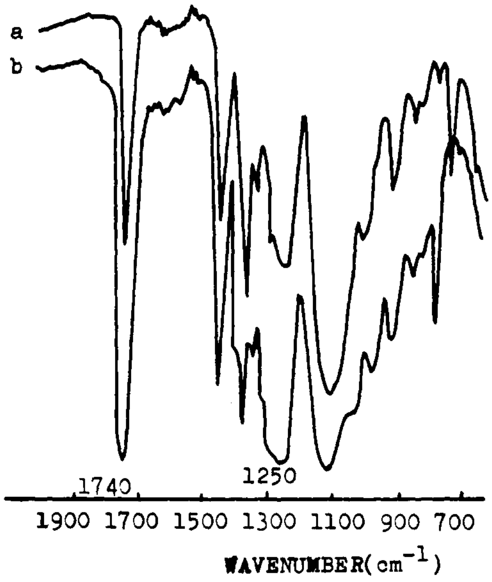

Figure 6. IR spectra of the copolymer: (a) methanol-soluble part; (b) methanol-insoluble part.

The copolymerization of PO and carbon dioxide can also be carried out in other solvents. The yield of the copolymer was greatly influenced by the solvent used, as shown in Table III. The activity sequence is as follows: 1,4-dioxane/benzene (1:1) > toluene > aliphatic hydrocarbon > ether, THF > CH_2Cl_2 > DMF, 2-butanone. This might be related to the solubility of CO_2 in various solvents. The structure of the copolymer was also influenced by the solvent used and the polymerization temperature.

In conclusion, the rare-earth coordination catalysts composed of $RE(P_{204})_3$, $Al(i\text{-}Bu)_3$, and glycerine are effective for the copolymerization of carbon dioxide and PO. The highest yield and intrinsic viscosity of the

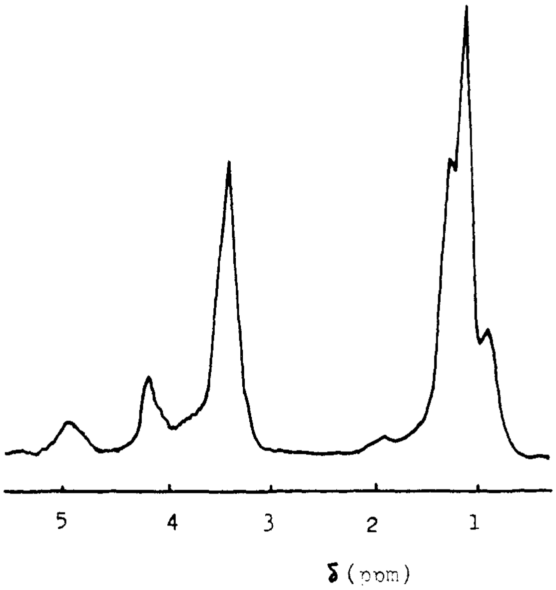

Figure 7. ^1H NMR spectrum of the methanol-insoluble copolymer.

copolymer reach more than 3000 g/mol of Y and 4.73 dL/g ($\bar{M}_n$ = 61 × 10^4), respectively. The most favorable conditions for the copolymerization of CO_2 and PO catalyzed by the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine system are as follows: Al/Y = 8; III/Al = 0.4–0.6; 60 °C; 1,4-dioxane/benzene, 1,4-dioxane/toluene, or 1,4-dioxane as solvent.

Characterization of the CO_2/PO Copolymer. The rare-earth copolymers obtained have a high molecular weight and a narrow molecular weight distribution. Table IV illustrates some properties of three typical specimens with different intrinsic viscosities. The data show that the copolymers are partly insoluble in methanol (40–75%). It has been found that the molecular weight and the carbonate unit content (CU %) of the methanol-insoluble portions are higher than those of the methanol-soluble portions. The IR spectra of the two parts are shown in Figure 6. Strong absorption bands at 1740 and 1250 cm^{-1} are due to the C=O and C–O stretching vibrations of the oxycarbonyloxy group, respectively.

The ^1H NMR spectrum (Figure 7) of the methanol-insoluble part shows chemical shifts from internal TMS at 1.3 ppm for CH_3, 3.5 ppm for CH + CH_2 in the PO unit, 4.2 ppm for CH_2 in the carbonate unit, and 5.0 ppm for CH in the carbonate unit. The carbonate unit content of the methanol-insoluble copolymer calculated from the ^1H NMR is in the range of 30–40%.

DTA-TGA analysis shows that the copolymers obtained are highly thermally stable. The decomposition temperature is more than 300 °C (Figure 8).

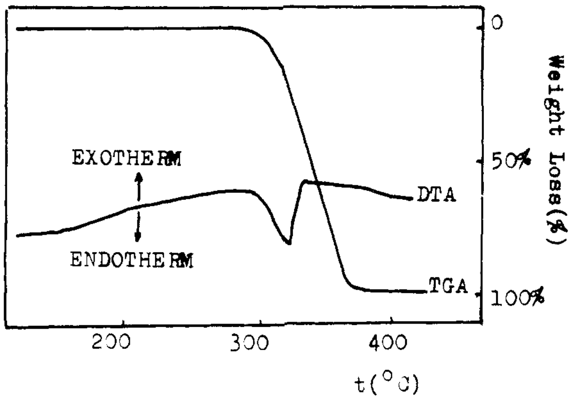

Figure 8. DTA-TGA analysis of the copolymer N_2; 10 °C/min.

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Registry No. $(PO)(CO_2)$ (copolymer), 25511-85-7; $Sc(P_{204})_3$, 22989-17-9; $Y(P_{204})_3$, 38326-06-6; $La(P_{204})_3$, 45324-95-6; $Nd(P_{204})_3$, 38326-04-4; $Eu(P_{204})_3$, 79950-28-0; $Gd(P_{204})_3$, 79950-29-1; $Tb(P_{204})_3$, 79950-30-4; $Dy(P_{204})_3$, 45324-92-3; $Ho(P_{204})_3$, 45324-94-5; $Er(P_{204})_3$, 79950-31-5; $Tm(P_{204})_3$, 26312-52-7; $Yb(P_{204})_3$, 38326-05-5; $Lu(P_{204})_3$, 79950-32-6; $Al(i\text{-}Bu)_3$, 100-99-2; H_2O, 7732-18-5; CH_3OH, 67-56-1; $HO(CH_2)_2OH$, 107-21-1; $CH_3CH(OH)CH_3$, 67-63-0; $n\text{-}C_4H_9OH$, 71-36-3; $(CH_3)_3COH$, 75-65-0; $HOCH_2C\equiv CCH_2OH$, 110-65-6; propylene glycol, 57-55-6; glycerine, 56-81-5; benzene, 71-43-2; tetrahydrofuran, 109-99-9; cyclohexane, 110-82-7; toluene, 108-88-3; 1,4-dioxane, 123-91-1; ether, 60-29-7.