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Synthesis and Characterization of Polymer-Supported Lanthanide Complexes and Butadiene Polymerization Based on Them

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ABSTRACT: Poly(styrene–acrylic acid)–lanthanide (Ln·PSAA) and poly(ethylene–acrylic acid)–neodymium (Nd·PEAA) complexes have been prepared and characterized. The infrared and X-ray photoelectron spectra indicate that the lanthanide complexes possess the bidentate carboxylate structure $\overline{\mathrm{Ln{-}O{\cdots}C(R){\cdots}O}}$ (see structure B in text). The catalytic behavior of the complexes has been described. The catalytic activities of Nd·PSAA and Nd·PEAA are much greater than that of the corresponding low molecular weight catalyst for butadiene polymerization. The activities of various individual lanthanide elements are quite different from one another. Neodymium shows the highest activity. Europium, samarium and the heavy elements exhibit very low or no activities. The cis-1,4 content of the polybutadiene obtained is not affected by different lanthanide elements in the series. The complex with the intermediate content of the functional group has a higher activity than the others. The polymer-supported lanthanide complexes having different constitutions have different catalytic activities. When the molar ratio of lanthanide to the functional group is ca. 0.2, the activity of the complex is in the optimum state. The activity is influenced by the dispersion of the lanthanide metal immobilized on the polymer chain. Catalytic activity can be improved by adding other metals to the catalyst system.

Introduction

The significant improvement in catalytic activity probably represents the single most important advantage of a supported catalyst. Even in the absence of a support, ordinary Ziegler–Natta catalysts are active; however, catalysts based on lanthanide complexes require an appropriate support for any significant polymerization activity. With this purpose in mind, we have paid a great deal of attention to polymer-supported metal complexes, especially to those with 4f electrons. Some polymer-supported lanthanide catalysts with high activity have been developed.[1-8]

In this paper, the synthesis and characterization of poly(styrene–acrylic acid)–lanthanide complexes (Ln·PSAA) and their catalytic behavior for butadiene polymerization are described.

Experimental Section

Materials. Analytically pure grade styrene and acrylic acid were purified by the usual procedures.[4] Poly(styrene–acrylic acid) (PSAA) was prepared by the radical copolymerization of styrene with acrylic acid using AIBN as initiator. Poly(ethylene–acrylic acid) (PEAA) was purchased from Polysciences Inc. and used directly. Analytically pure grade toluene used as catalyst solvent was refluxed with K–Nd alloy and distilled before use. Commercially pure grade hexane used as polymerization solvent was dried over active alumina for a week. Butadiene was dried over active alumina before use. Triisobutylaluminum, diethylaluminum chloride, and diisobutylaluminum hydride were purchased from Fluka AG. The other solvents and reagents were dried by proper methods and distilled as required.

Preparation of Ln·PSAA. A solution of lanthanide chloride (0.2 g) in methanol (20 mL) was added to a solution of PSAA (2 g) in 100 mL of methyl ethyl ketone (MEK) at room temperature. Then a solution of ammonium hydroxide (0.4 mL) in MEK (50 mL) was added dropwise into the mixture with stirring. After the addition was complete, the reaction system was allowed to stand for 1 h. The product, which was insoluble in the reaction medium, was filtered out immediately, washed with distilled water until no chloride ion could be detected by silver nitrate titration in the filtrate, and dried under vacuum at 40 °C for 48 h.

Preparation of Nd–Fe(or Na)·PSAA. Nd–Fe (or Na)·PSAA was prepared by reacting PSAA with neodymium chloride and iron chloride (or sodium chloride) at room temperature. The other process was similar to that in Ln·PSAA.

Preparation of Nd·PEAA. PEAA was dissolved in THF–chlorobenzene (3:1) by heating at 64 °C. A solution of neodymium chloride in methanol was added to this solution, and then a solution of ammonium hydroxide in THF was added dropwise into the mixture with stirring. After this, the reaction mixture was allowed to react for 2 h. The mixture was poured into methanol, filtered, washed with methanol until there was an absence of chloride ion in the filtrate, and dried under vacuum at 40 °C for 48 h.

Polystyrene-*graft*-poly(acrylic acid)–neodymium (Nd·PS-*g*-PAA) and polypropylene-*graft*-poly(acrylic acid)–neodymium (Nd·PP-*g*-PAA) were prepared according to the literature.[7]

Butadiene Polymerization and Analysis of Polymer. The polymerization was performed in 50 mL-ampules under an atmosphere of nitrogen. Moisture and air were carefully excluded from all the polymerization processes. The polymerization was terminated by adding an ethanol solution containing phenyl-β-naphthylamine. The polymer obtained was precipitated with an excess of ethanol and dried under vacuum below 40 °C to constant weight.

The intrinsic viscosity $[\eta]$ and microstructure of the polymer were determined as described earlier.[4]

Results and Discussion

1. Characterization of Polymer-Supported Lanthanide Complexes.

The characteristic parameters of the polymer-supported lanthanide complexes are shown in Table I. It is clear from Table I that the resulting products of reacting PSAA and PEAA with $LnCl_3$ show the absence of chloride ion. This indicates that the chlorine in $LnCl_3$ is exchanged by the carboxyl group in PSAA and PEAA to form a macromolecular carboxylate complex with Ln as a cross-linking point.

In the IR spectrum of PSAA (Figure 1a), the bands at 1700 and 1265 cm^{-1} are attributed to ν(C=O) and ν(C–O) of the carboxyl group in PSAA. In the case of PEAA, similar bands were also observed (Figure 1b). In the IR spectra of Ln·PSAA and Nd·PEAA, new bands appear in the regions 1540–1520 and 1420–1400 cm^{-1} (Table I), which are assigned as $\nu_{as}(COO^-)$ and ν_s (COO^-), respectively.

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Table I. Characteristic Parameters of Polymer-Supported Ln Complexes

Ln·PSAA	func group (mmol/g)	elem anal. (mmol/g) Ln	elem anal. (mmol/g) Cl	Ln (or Na)/func group (mol ratio)	$\nu_{as}(COO^-)$ (cm^{-1})	$\nu_s(COO^-)$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
La	2.66	0.48	0.00	0.18	1530	1401	129
Ce	2.66	0.47	0.00	0.18	1532	1410	122
Pr	2.66	0.41	0.00	0.15	1527	1410	117
Nd	2.66	0.46	0.00	0.17	1534	1413	121
Sm	2.66	0.40	0.00	0.15	1532	1415	117
Eu	2.66	0.48	0.00	0.18	1526	1410	116
Gd	2.66	0.44	0.00	0.17	1530	1410	120
Tb	2.66	0.44	0.00	0.17	1530	1420	110
Dy	2.66	0.47	0.00	0.18	1530	1420	110
Ho	2.66	0.47	0.00	0.18	1538	1420	118
Er	2.66	0.44	0.00	0.17	1533	1420	113
Tm	2.66	0.44	0.00	0.17	1531	1420	111
Yb	2.66	0.41	0.00	0.15	1532	1420	112
Lu	2.66	0.42	0.00	0.16	1540	1420	120
Na·PSAA	2.66	0.44	0.00	0.17	1576	1418	158
Nd·PEAA	2.53	0.44	0.00	0.17	1540	1420	120
Na·PEAA	2.53	0.43	0.00	0.17	1570	1420	150

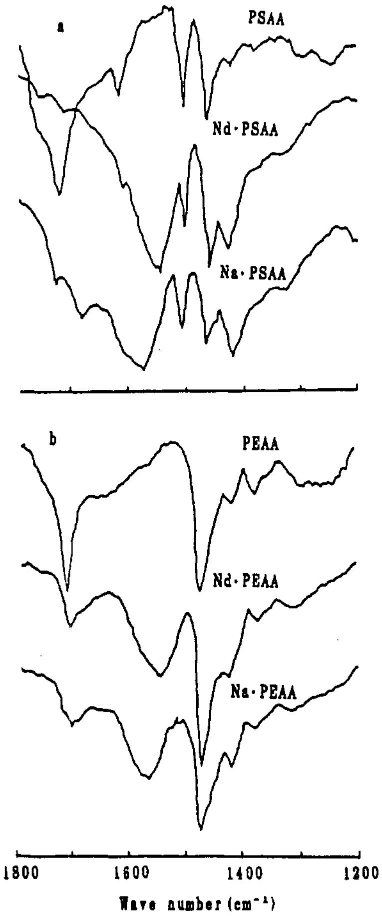
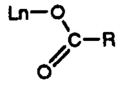


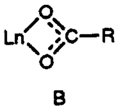
Figure 1. IR absorption spectra of polymer supports and their metal complexes.

These data reveal the coordination of the oxygen atom of the ligand to the central ion.

Two modes of bonding through the carboxyl group are regarded as the most probable ones in the case of Ln·PSAA and Nd·PEAA formation:



A



B

The difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, $\Delta\nu$, reflects the symmetry of the carboxyl group on the complex formation and the bond covalency. The smaller the $\Delta\nu$ value, the higher is the symmetry of the carboxyl group.

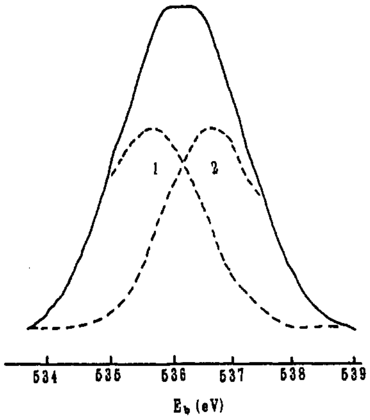
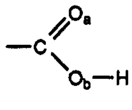


Figure 2. $O1_s$ binding energy of PEAA.

From the data shown in Table I, it is seen that the $\Delta\nu$ values of Ln·PSAA and Nd·PEAA are all smaller than those of Na·PSAA and Na·PEAA, respectively, so it is reasonable to conclude that Ln·PSAA and Nd·PEAA possess the bidentate carboxylate structure B.[8]

The bidentate carboxylate structure B was also confirmed by the X-ray photoelectron spectrum of the polymer-supported lanthanide complex. The O_{1s} binding energy in PEAA shows two peaks (Figure 2), indicating that the chemical environments of the two oxygen atoms in the carboxyl group are different from one another. The carboxyl group has the structure



C

Peak 1 (535.8 eV) in Figure 2 is due to the binding energy of O_a in structure C; peak 2 (536.8 eV) in Figure 2 corresponds to the binding energy of O_b in structure C. The X-ray photoelectron spectrum of Nd·PEAA exhibits three peaks (Figure 3): peak 1 (535.8 eV), corresponding to O_a in structure C; peak 2 (536.8 eV), corresponding to O_b in structure C (in the present experiment, since the COOH/Nd molar ratio is 6.7, unreacted carboxyl groups remain in Nd·PEAA); peak 3 (537.8 eV), corresponding to O in structure B in which the two oxygen atoms are in an identical environment.

2. Catalytic Activities of Polymer-Supported Lanthanide Complexes. Nd·PSAA and Nd·PEAA combined with $Al(i\text{-}Bu)_3$ and $AlEt_2Cl$ can give highly active catalysts for butadiene polymerization. As indicated in Table II,

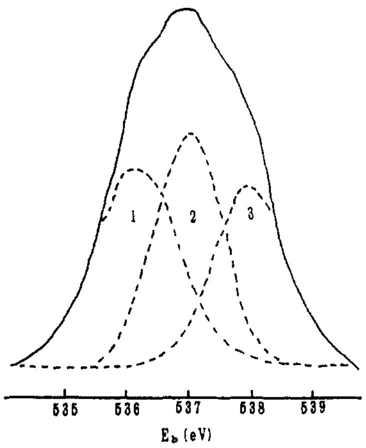


Figure 3. O1s binding energy of Nd·PEAA.

Table II. Comparison of the Activities of Various Neodymium Complexes[a]

system	Nd/Bd (μmol ratio)	conv (%)
Nd·PSAA–Al(*i*-Bu)$_3$–AlEt$_2$Cl	0.3	94
Nd·PEAA–Al(*i*-Bu)$_3$–AlEt$_2$Cl	0.3	96
Nd·AA–Al(*i*-Bu)$_3$–AlEt$_2$Cl	0.6	4

[a] Polymerization conditions: Al/Nd (mol ratio) = 200; Cl/Nd (atom ratio) = 3; 50 °C; 6 h. Nd·AA = neodymium acetate; Bd = butadiene.

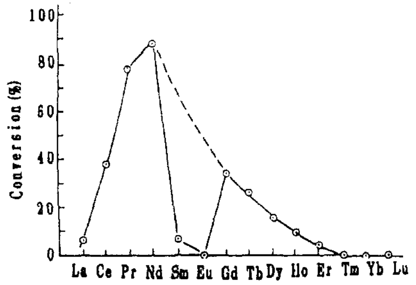


Figure 4. Activity of various lanthanide elements in Ln·PSAA systems for polymerizing butadiene Polymerization conditions: Ln/Bd (mol/g) = 2 × 10^{-7}; Al/Ln (mol ratio) = 200; Cl/Ln (atom ratio) = 3.5; 50 °C; 6 h; Bd = butadiene.

the catalytic activities of Nd·PSAA and Nd·PEAA are much greater than that of the corresponding low molecular weight catalyst for butadiene polymerization. Nevertheless, the activities of various individual lanthanide elements are quite different from one another (Figure 4). It is clear from Figure 4 that a peak in activity is observed for neodymium. Europium, samarium, and the heavy elements exhibit very low or no catalytic activities. The different activities of various lanthanide elements reveal the difference in complexing ability due to the electronic structure or the number of 4f orbital electrons in each kind of element in the series. The cis-1,4 content of polybutadiene produced by different lanthanide elements is the same, more than 98% (Table III). The same stereoregularity of polybutadiene prepared with different lanthanide elements reflects the similarity in chemical nature of 4f electrons in all the lanthanides.

3. Effect of the Content of the Functional Group on the Activity. As shown in Table IV, the species with the intermediate content of the functional group has a higher activity than the others. At the higher content of the functional group, the activity is not as good as that of the one with low functional group content.

4. Effect of the Constitution of the Polymer Support. The neodymium complexes with polymer supports having different constitutions are summarized in Table V. The formulas of the supports shown in Table V are as follows:

Table III. Microstructure of Polybutadiene with Ln·PSAA[a]

lanthanide	microstructure (%) cis-1,4	trans-1,4	1,2
La	98.4	0.8	0.8
Ce	98.6	0.9	0.5
Pr	98.7	0.9	0.4
Nd	98.6	0.8	0.6
Sm	99.0	0.7	0.3
Gd	99.3	0.4	0.3
Tb	98.4	1.1	0.5
Dy	98.4	0.9	0.7
Ho	98.4	1.0	0.6
Er	98.3	0.6	1.1

[a] Polymerization conditions are the same as in Figure 4.

Table IV. Effect of the Content of the Functional Group in Nd·PSAA on the Activity[a]

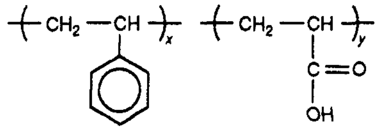
COOH content (mmol/g)	Nd/COOH (mol ratio)	conv (%)
1.96	0.19	84
2.07	0.18	92
2.67	0.19	94
3.54	0.19	78
3.68	0.20	74

[a] Polymerization conditions: Nd/Bd (μmol/g) = 0.3; Cl/Nd (mol ratio) = 3.5; Al/Nd (mol ratio) = 200; 50 °C; 6 h. Bd = butadiene.

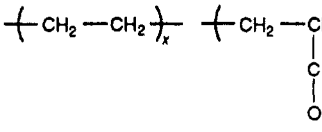
Table V. Effect of the Constitutions of the Polymer Supports

complex	Nd/Bd (μmol/g)	Cl/Nd (mol/mol)	Al/Nd (mol/mol)	temp (°C)	time (h)	conv (%)
Nd·PSAA[a]	0.3	3.5	200	50	6	94
Nd·PEAA[b]	0.3	3	200	50	6	96
Nd·PS-*g*-PAA[b]	0.3	3	200	50	6	trace
Nd·PE-*g*-PAA[c]	5	3	200	50	6	trace
(PS-CO$_2$)$_3$Nd[d]	25 mol/g	2	40	70	48	44

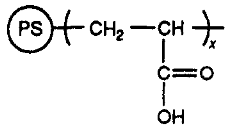
[a] Third component, benzyl chloride; cocatalyst, Al(*i*-Bu)$_3$. [b] Third component, AlEt$_2$Cl; cocatalyst, Al(*i*-Bu)$_3$. [c] Third component, triphenylchloromethane; cocatalyst, Al(*i*-Bu)$_3$. [d] Third component, AlEt$_2$Cl; cocatalyst, Al(*i*-Bu)$_3$; ref 9.



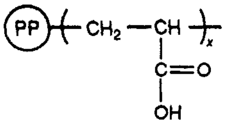
PSAA (I)



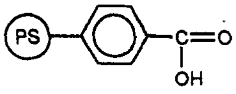
PEAA (II)



PS-*g*-PAA (III)



PP-*g*-PAA (IV)



PS–CO$_2$H (V)

For the grafted copolymers III and IV, the sequence of carboxyl group is equal to that of the homopolymer of acrylic acid. The carboxyl groups in polymers I and II are bonded to the main chain of PSAA (or PEAA). Polymer V is different from polymers I and II, in that polymer V is carboxylated DVB-cross-linked polystyrene. Different polymer-supported neodymium complexes have different catalytic activities in butadiene polymerization in spite of the fact that the support polymers contain the same

Table VI. Effect of the Ratio of the Metal Loading to the Functional Group on the Activity[a]

COOH content in PSAA (mmol/g)	quantity of bound Nd (mmol/g)	Nd/COOH (mol ratio)	conv (%)
1.92	0.31	0.16	74
1.92	0.39	0.20	90
1.92	0.62	0.32	60
2.67	0.51	0.19	94
2.67	0.61	0.23	90
2.67	0.78	0.29	82

[a] Polymerization conditions: Nd/Bd (μmol/g) = 0.3; Cl/Nd (mol ratio) = 3.5; Al/Nd (mol ratio) = 200; 50 °C; 6 h.

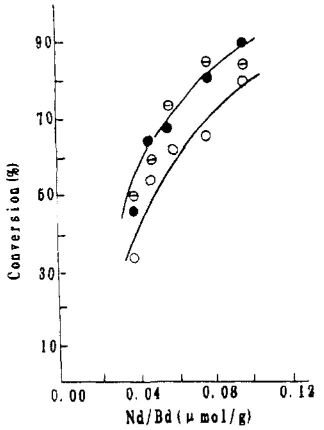


Figure 5. Comparison of the activity of various metal complexes with PSAA: (●) Nd–Fe·PSAA; (⊖) Nd–Na·PSAA; (○) Nd·PSAA

functional group, i.e., the carboxyl group. Nd·PSAA and Nd·PEAA show appreciably high activity, and the catalytic activities of the others are very low, as shown in Table V.

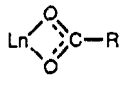
5. Effect of the Ratio of the Metal Loading to the Functional Group. As indicated in Table VI, when the Nd/COOH molar ratio in Nd·PSAA is ca. 0.20, the activity of Nd·PSAA is in an optimum state. This suggests that the environment of the metal neodymium ions in Nd·PSAA is of great advantage in forming the active centers with aluminum alkyl and the third component.

6. Effect of the Dispersion of the Metal Fixed on the Polymer Chain. We have synthesized the Nd and Fe(or Na)-containing bimetallic complexes, Nd–Fe·PSAA and Nd–Na·PSAA, to examine the effect of the dispersions of the metal anchored on the polymer chain on the activity. The purpose of the addition of the other metals is to govern the dispersion of neodymium acting as active species and then to improve its activity. As was expected, the Fe·PSAA–Al(i-Bu)$_3$–AlEt$_2$Cl (different from the active system Fe·PSAA–Phen–Al(i-Bu)$_3$) and Na·PSAA–Al(i-Bu)$_3$–AlEt$_2$Cl systems showed no activity for butadiene polymerization under the given experimental conditions, whereas the Nd·PSAA–Al(i-Bu)$_3$–AlEt$_2$Cl system can catalyze the polymerization of butadiene. It may be considered that Fe and Na only play the part of adjusting the dispersion of Nd immobilized on the polymer chain and Nd serves as the active centers. It is obvious in Figure 5 that the activities of the Nd–Fe·PSAA and Nd–Na·PSAA systems were both higher than that of the Nd·PSAA system. It is reasonable that such a high activity for the Nd–Fe·PSAA and Nd–Na·PSAA systems must be attributed to the efficient dispersion of Nd atoms supported on the PSAA chain by adding Fe and Na.

Conclusions

The elemental analyses indicate the absence of chlorine ion in all the polymer-supported lanthanide complexes. It is considered that the chlorine in LnCl$_3$ is exchanged by the carboxyl group in the polymer supports to form a macromolecular carboxylate complex with Ln as the cross-linking point.

Based on the infrared and X-ray photoelectron spectra in Ln·PSAA and Nd·PEAA, all the lanthanide complexes possess the bidentate carboxylate structure:



The activities of polymer-supported neodymium complexes are much greater than that of the corresponding low molecular weight catalyst for butadiene polymerization, so it is believed that such a high activity in polymer-supported neodymium complexes may be due to the efficient dispersion of neodymium metal along the polymer chain.

The different activities of various individual lanthanide elements reveal the difference in complexing ability due to the electron structure of the number of 4f orbital electrons in each kind of element in the series. The same microstructure of polybutadiene obtained with different lanthanide elements reflects the similarity in chemical nature of 4f electrons in all the lanthanides.

The activities of the polymer-supported lanthanide are affected to a great extent by the following factors: the content of the functional group, the constitution of the polymer supports, the ratio of the metal loading to the functional group, and the dispersion of the metal supported on the polymer.

Adding other metals (Fe or Na) to the lanthanide catalyst system can improve the dispersion of the metal on the polymer chain and then enhance the activity of the system.

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