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CATALYTIC ACTIVITY OF POLYMER-SUPPORTED NEODYMIUM COMPLEXES IN THE POLYMERIZATION OF BUTADIENE

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ABSTRACT

The IR spectra of neodymium complexes supported on styrene-acrylic acid copolymer were investigated. The complexes possess a bidentate carboxylate structure, and the Nd–O bond in the complexes is highly covalent. The effect of the nature and constitution of the supported neodymium complexes on their activity in butadiene polymerization was studied. The copolymer was prepared in THF or dioxane was better for the synthesis of highly active supported complexes. Polymer-supported neodymium complexes containing about 12 wt% of –COOH gave optimum catalytic activity at a Nd/–COOH mole ratio of 0.20.

INTRODUCTION

Since 1980 we [1-5] have reported on polymer-supported metal (Ln, Fe) catalysts which possess good catalytic activity and stereospecificity for the polymerization of conjugated dienes. It is well known that the efficiency of the catalyst active center is influenced by the nature and the valence state of the transition metal, the type of ligands attached to the transition metal, the type of organometallic compound, and the catalyst morphology. The ability to manipulate these parameters effectively has led to the successful development of new, more highly active catalysts. In comparison with low molecular weight metal catalysts, the environment of the metallic ions in the active centers of polymer-metal catalysts is influenced by the polymer ligand, so that the latter catalyst is different in nature and efficiency from that of the former. We have synthesized neodymium complexes with styrene-acrylic acid copolymer as the ligand and studied the nature of the complexes, the constitution, and the relationship between them and their activity in the butadiene polymerization.

EXPERIMENTAL

Materials

Chemically pure grade benzyl chloride was distilled before use. Analytically pure grade toluene was refluxed with K-Na alloy and distilled before use. Commercially pure grade hexane was dried over active alumina for a week. Neodymium chloride ($NdCl_3 \cdot 6H_2O$) and anhydrous neodymium acetate were prepared according to the literature [6, 7]. Triisobutylaluminum, triethylaluminum, and diethylaluminum chloride were obtained from Fluka AG. Butadiene was dried over active alumina before use. Styrene-acrylic acid copolymer (SAAC) was prepared according to methods A [8] and B [9]. In Method A, the copolymerization of styrene and acrylic acid in bulk was carried out at 60°C. In Method B, styrene was copolymerized with acrylic acid in electron-donor solvents at 40°C. The initiator used was azobisisobutyronitrile. Ethylene-acrylic acid copolymer (EAAC) was obtained from Polysciences, Inc., Warrington, Pennsylvania, U.S.A.

Preparation of Neodymium Complexes Supported on Styrene-Acrylic Acid Copolymer (SAAC·Nd)

A solution of neodymium chloride in methanol was added to a solution of SAAC in methyl ethyl ketone (MEK) at room temperature. Then a solution of ammonium hydroxide in MEK was added dropwise into the mixture with stirring. After this, 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 in the filtrate, and dried under vacuum at 60°C for 48 h.

Preparation of Neodymium Complexes Supported on Ethylene-Acrylic Acid Copolymer (EAAC·Nd)

EAAC 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 the solution of ammonium hydroxide in THF was added dropwise with stirring. The reaction mixture was immediately poured into methanol, filtered off, washed with methanol to the absence of Cl^-, and dried under vacuum at 40°C for 24 h.

Polymer-supported neodymium complexes with different contents of Nd were prepared by changing the Nd/—COOH ratio. The amount of Nd in the complexes was determined by complexometric titration after ignition. The IR absorption spectra of the supports and their neodymium complexes were taken in KBr pellets with a Perkin-Elmer infrared spectrophotometer.

Polymerization Procedure and Analysis of Polymer

The polymerization was carried out in 50-mL ampules under Ar. 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 [η] and the microstructure of the polymers obtained were determined according to a previously reported method [5].

RESULTS AND DISCUSSION

Characteristics of Polymer-Supported Neodymium Complexes

Since elemental analysis of the reaction products of the supports (SAAC, EAAC) with $NdCl_3$ showed the absence of Cl^-, we concluded that the chlorine in $NdCl_3$ had been exchanged by the carboxyl groups in the support to form macromolecular carboxylate complexes with Nd as the crosslinking point.

The IR spectra of SAAC·Nd and EAAC·Nd (Fig. 1a and 1b) show that new bands appear at 1550 and 1540 cm^{-1} as well as at 1426 and 1420 cm^{-1}, which represent antisymmetric and symmetric stretching vibrations of $-COO^-$ groups due to the formation of the complexes. These are similar

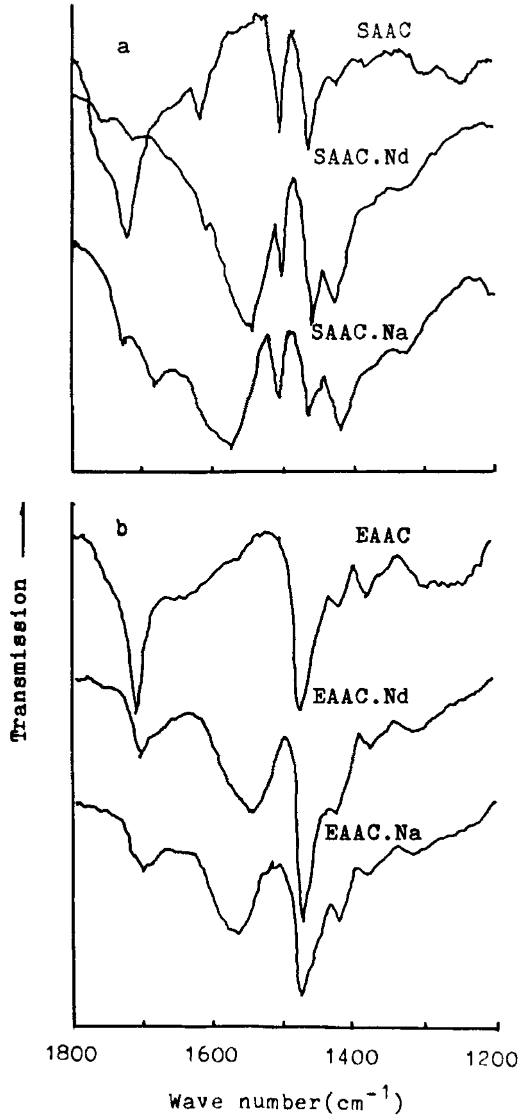
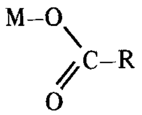
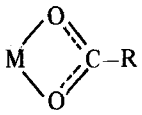


FIG. 1. IR absorption spectra of polymer supports and their metal complexes.

to those of low molecular weight rare-earth carboxylate complexes. There are two possible structures of the rare earth complexes with carboxylic acids [10-14]:



(a)



(b)

Two bands, $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, which are close to each other, correspond to bidentate bonding (b), whereas those more distant are due to monodentate bonding (a). It is well known that an increase in covalency of the metal-oxygen bonds is always accompanied by an increase in $\nu_s(COO^-)$ and a decrease in $\nu_{as}(COO^-)$. From the data in Table 1, we can infer that the polymer-supported neodymium complexes possess the bidentate carboxylate structure and that the metal-oxygen bonds in the complexes are highly covalent.

One of the requirements for the formation of the active center is the halogenation of rare earth ions by exchange between Cl in alkylaluminum halide and carboxylate for the rare-earth ternary systems used in the polymerization of conjugated dienes [15-17]. The covalency of the metal-oxygen bond in the support complex makes the exchange reaction easier. This point is fully proved by the higher catalytic activity of the complexes in butadiene polymerization (Table 2). Based on the investigation of IR spectra about rare-earth propionate, Petrov and coworkers [18] pointed out that the nature of the Ln—O bond did not change essentially from acetate to propionate, and the covalency of the bond was not high. The data in Table 2 demonstrate that neodymium acetate gave low catalytic activity. It is quite evident that the lower catalytic activity is related to the low covalency of the Nd—O bond in neodymium acetate. The polymer-supported neodymium complex catalysts retain the characteristics of low molecular weight rare-earth catalysts, so the polybutadiene obtained has a higher *cis*-1,4 content.

Effects of the Constitution on the Catalytic Activity of Polymer-Supported Neodymium Complexes

In order to find out the relations between the constitution and the catalytic activity of polymer-supported neodymium complexes, three groups of SAAC

TABLE 1. Vibration Frequencies $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ for Polymer-Supported Complexes with Sodium and Neodymium

	SAAC			EAAC		
Compound	$\nu_{as}(COO^-)$, cm^{-1}	$\nu_s(COO^-)$, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu_{as}(COO^-)$, cm^{-1}	$\nu_s(COO^-)$, cm^{-1}	$\Delta\nu$, cm^{-1}
Sodium salt	1576	1418	158	1570	1420	150
Complex with neodymium	1550	1426	124	1540	1420	120

TABLE 2. Effect of Various Neodymium Complexes on the Polymerization of Butadiene[a]

Catalyst system	Nd/Bd, μmol/g	Cl/Nd, mol ratio	Al/Nd, mol ratio	Conversion, %	$[\eta]$, dL/g	Microstructure, %		
						cis-1,4	*trans*-1,4	1,2
SAAC·Nd-$PhCH_2Cl$-$Al(i\text{-}C_4H_9)_3$	0.2	3.5	200	88	8.5	98.6	0.9	0.5
	0.3	3.5	200	94	6.3	98.6	0.9	0.5
	0.3	3.5	100	82	9.4	98.5	0.8	0.7
SAAC·Nd-$PhCH_2Cl$-$Al(C_2H_5)_3$	0.3	3.5	200	78	6.5	98.2	1.0	0.8
SAAC·Nd-$PhCH_2Cl$-$Al(i\text{-}C_4H_9)_2H$	0.3	3.5	200	66	4.9	98.1	1.0	0.9
EAAC·Nd-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$	0.3	3	200	96		98.6	1.1	0.3
	0.6	3	100	85	5.3	98.1	1.2	0.7
$Nd(CH_3COO)_3$-$Al(C_2H_5)_2Cl$-$Al(i\text{-}C_4H_9)_3$	0.6	3	100	4	6.2	98.7	1.0	0.3
$Nd(CH_3COO)_3$-$PhCH_2Cl$-$Al(iC_4H_9)_3$	0.6	3	100	2	—	—	—	—

[a] Polymerization conditions: monomer concentration, 10 g/100 mL hexane; catalyst aging concentration, 10 μmol/mL toluene; 50°C; 6 h.

TABLE 3. Relationship between SAAC·Nd Properties and Catalytic Activity[a]

Run no.	Synthetic method for SAAC	Functional groups		Quantity of bound metal		Conversion of butadiene, %
		wt%	mmol/g	mmol/g	mol/mol of functional group	
74	A	8.8	1.96	0.37	0.19	84
73				0.50	0.26	82
72				0.57	0.29	76
71				0.63	0.32	60
82		11.5	2.55	0.45	0.18	87
81				0.60	0.24	80
83				0.73	0.29	72
85				0.80	0.31	64
95		15.9	3.54	0.45	0.13	31
94				0.60	0.17	64
93				0.67	0.19	78
92				1.00	0.28	48
17	B (solvent, dioxane)	9.3	2.07	0.37	0.18	92
18				0.49	0.24	90
19				0.64	0.31	82

202		11.9	2.65	0.52	0.20	94
203				0.61	0.23	92
204				0.69	0.26	85
205				0.85	0.32	62
214		15.2	3.38	0.57	0.17	84
213				0.76	0.23	80
212				0.83	0.25	76
161	B (solvent, THF)	8.6	1.92	0.31	0.16	74
162				0.39	0.20	90
163				0.62	0.32	60
272		12.0	2.67	0.51	0.19	94
273				0.61	0.23	90
274				0.78	0.29	82
181		16.6	3.68	0.65	0.18	58
182				0.74	0.20	74
183				0.91	0.25	54

[a] Polymerization conditions: monomer concentration, 10 g/100 mL hexane; Nd/Bd 0.3 μmol/g; third component, $PhCH_2Cl$; Cl/Nd (mole ratio) = 3.5; cocatalyst, $Al(i\text{-}C_4H_9)_3$; Al/Nd (mole ratio) = 200; catalyst aging concentration, 10 μmol/mL toluene; 50°C; 6 h.

TABLE 4. Relationship between EAAC•Nd Properties and Catalytic Activity[a]

	Functional groups		Quantity of bound metal		
Run no.	wt%	mmol/g	mmol/g	mol/mol of functional group	Conversion of butadiene, %
141	11.4	2.53	0.14	0.06	35
142			0.39	0.15	50
143			0.44	0.17	85
144			0.69	0.27	57

[a]Polymerization conditions: monomer concentration, 10 g/100 mL hexane; Nd/Bd = 0.6 μmol/g; third component, $Al(C_2H_5)_2Cl$, Cl/Nd (mole ratio) = 3; cocatalyst, $Al(i\text{-}C_4H_9)_3$; Al/Nd (mole ratio) = 100; catalyst aging concentration, 10 μmol/mL toluene; 50°C; 6 h.

were synthesized by the two different methods and different contents of –COOH. It is clear from the results in Table 3 that no matter whether Method A or B was used in the synthesis of SAAC, as long as the Nd/–COOH mole ratio in the SAAC•Nd was about 0.20, the catalytic activity was optimum. This may indicate that the environment of the neodymium ions in SAAC•Nd is favorable for the formation of the active centers with the third component (alkyl chloride or aluminum alkyl halide) and alkyl aluminum. Among the three groups, the one with intermediate content of functional groups (about 12 wt%) has higher activity than the one with a higher functional group content (about 16 wt%). At the higher content of functional groups, even if the Nd/–COOH molar ratio was 0.20, the activity was not as good as that of the one with low content.

Obviously, for the higher content of functional groups, we must increase the content of bound neodymium (see Runs 93, 82, 74; 182, 272, 162; 214, 202, 17) in order to maintain the ratio of neodymium and functional group content at 0.20. It is evident that the increase in the bound neodymium increases the amount of Nd per unit support volume, and a portion of the Nd is embedded, while only the Nd metal on the surface will be active, as usually occurs in heterogeneous catalysts. When SAAC was prepared in the presence of either THF or dioxane, the neodymium complexes had higher activity.

EAAC•Nd also shows a similar regularity in butadiene polymerization (Table 4). At high catalytic activity the Nd/–COOH molar ratio was 0.17, i.e., nearly 0.20. As the Nd content in EAAC•Nd increases, the catalytic activity reaches a maximum value. When the neodymium content is much higher, the neodymium function cannot have its full catalytic effect, as has been discussed briefly above. At much lower Nd content, the amount of Nd per unit support volume is very low, and the active centers formed are smaller, so that the activity is low.

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