Polymerization of dienes to *trans*-1,4-polydienes with f-orbital transition-metal compounds and organoaluminium compounds

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Isoprene and butadiene have been polymerized with various f-orbital transition-metal compounds and organoaluminium compounds. The microstructure of polydienes was determined by infra-red spectroscopy and/or ^{13}C nuclear magnetic resonance spectroscopy and found to be predominantly *trans*-1,4 structure, especially over 90% *trans*-1,4 units for polyisoprene. The conversion and/or *trans*-1,4 content of polyisoprene were affected by the order of addition of components, ageing time, structure of transition metal and organoaluminium compounds, and solvent.

(Keywords: polyisoprene; polybutadiene; lanthanide compounds; microstructure; ageing time; Ziegler–Natta catalysts)

INTRODUCTION

There has been considerable interest in the polymerization of 1,3-dienes with catalysts derived from lanthanide compounds during the last few years[1–3]. The lanthanides (rare-earth metal compounds), which have unique and interesting stereochemical activities in contrast to the conventional d-orbital transition metal compounds, are a relatively new family of coordination catalysts for diene polymerization. A series of high-activity lanthanide catalysts were described[3] but still better lanthanide catalysts are needed to produce new, improved and lower-cost polydienes.

This report describes some aspects of the stereospecific polymerization of dienes with various f-orbital transition-metal compounds and alkylaluminium compounds. The effects of the order of addition of components, ageing time, structure of catalyst components and solvent on the conversion and microstructure of polydienes have been examined.

EXPERIMENTAL

Materials

Butadiene was obtained from the Korea Synthetic Rubber Co., and was purified by passing it through three successive columns containing KOH, Drierite and P_2O_5 respectively. Isoprene (Tokyo Kasei Co., Japan) was refluxed with sodium metal for 3 h and distilled under a dried nitrogen atmosphere. Toluene and n-hexane used as polymerization solvents were purified by a method described elsewhere[4].

Diethylaluminium chloride (DEAC) and tri-isobutylaluminium (TIBA) were purchased from Tokyo Kasei Co., Japan, and triethylaluminium (TEA), ethylaluminium dichloride (EADC) and ethylaluminium sesquichloride (EASC) were obtained from the Korea Petrochemical Co. The f-orbital transition-metal compounds (FTM) of $CeCl_3$, $Ce(acac)_3$, $GdCl_3$, $LuCl_3$, $NdCl_3{\cdot}6H_2O$, $PrCl_3{\cdot}6H_2O$ and $UO_2(C_2H_3O_2)_2{\cdot}6H_2O$ were purchased from PCR Co. and Alfa Products, Morton Thiokol Inc., USA, and dried in a vacuum oven at 70°C.

Polymerization procedures

Polymerization was carried out in a 200 ml glass reactor under dry nitrogen with a slightly positive pressure. The reactor was dried in an oven at 150°C and assembled while hot and flushed several times with dry nitrogen. All f-orbital transition-metal compounds and organoaluminium compounds were handled in an Atmos bag under an inert atmosphere of dry nitrogen.

The reagents were introduced into the reactor in the following order: the transition-metal compound was always added first, followed by either monomer or organoaluminium compound according to the order of addition.

The polymerization reaction was carried out at 20°C for a given time and terminated by adding methanol containing an antioxidant of *N*-phenyl-β-naphthylamine. The resulting polymer was then dried to constant weight under vacuum at 40°C and the percentage conversion was

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Table 1 Effects of order of addition on conversion and microstructure of polyisoprene

Transition-metal compounds	Addition method A		Addition method B		
	Conversion (%)	*Trans*-1,4 (%)	Ageing time (min)	Conversion (%)	*Trans*-1,4 (%)
$Ce(acac)_3$	83.6	94	2	46.9	97
$GdCl_3$	94.9	93	120	9.2	–
$LuCl_3$	55.0	88	120	100.5	92

[Isoprene] $=2.0\pm0.1\ \mathrm{mol\,l^{-1}}$, [FTM] $=(1.36\pm0.03)\times10^{-3}\ \mathrm{mol\,l^{-1}}$, [DEAC]/[FTM] $=20.0\pm0.5$; temperature 20°C; time 3 h
Addition method A: FTM + isoprene + DEAC
Addition method B: FTM + DEAC + isoprene

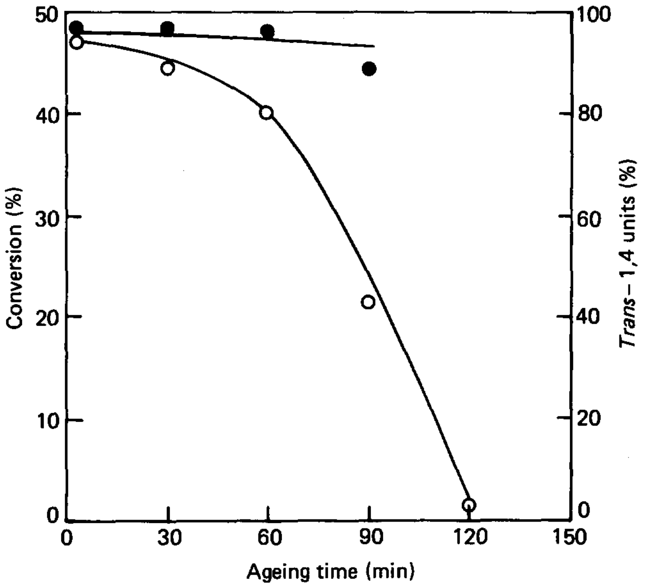

Figure 1 Effects of ageing time on conversion (○) and microstructure (●) of polyisoprene. [Isoprene] $=2.0\pm0.1\ \mathrm{mol\,l^{-1}}$, [$Ce(acac)_3$] $=(1.36\pm0.03)\times10^{-3}\ \mathrm{mol\,l^{-1}}$, [DEAC]/[$Ce(acac)_3$] $=20.0\pm0.5$; temperature 20°C; time 3 h

obtained gravimetrically after correction for the catalyst residues.

Polydiene characterizations

Microstructure of polydienes was determined with films on KBr plates using an i.r. spectrophotometer (Beckman IR 4250) according to the method of Binder and Ransaw[5]. ^{13}C n.m.r. (Varian FT-80) was also used to confirm the microstructure by the method of Duch and Grant[6].

RESULTS AND DISCUSSION

Microstructure of polydienes

In the i.r. spectrum obtained for the polyisoprene, the absence of the characteristic i.r. band at 910 $\mathrm{cm^{-1}}$ for the 1,2 unit as well as the absence of the band at 1130 $\mathrm{cm^{-1}}$ for the *cis*-1,4 unit indicated that the contents of 1,2 and *cis*-1,4 units were negligibly small. The chemical shift data of ^{13}C n.m.r. showed that polyisoprene obtained with $Ce(acac)_3$ and DEAC had *trans*-1,4 structure[7]. The polybutadiene obtained with various f-orbital transition-metal compounds and organoaluminium compounds also had high *trans*-1,4 structure judging from the intensities at 738, 911 and 967 $\mathrm{cm^{-1}}$, which are characteristic i.r. peaks of *cis*-1,4, 1,2 and *trans*-1,4 structures (see *Table 2*).

Although it has been well established that polydienes obtained with various lanthanide catalysts developed by Hsieh[3] have predominantly *cis*-1,4 form, we could obtain polydienes with high content of *trans*-1,4 unit, especially over 90% *trans*-1,4 structure for polyisoprene with various f-orbital transition-metal compounds and organoaluminium compounds. This difference in microstructure of polydienes might be due to the structure of catalyst components and various reaction conditions.

Order of addition of reaction components

It is well known that the order of addition of monomer, transition-metal compound and organoaluminium compound to the reactor greatly affected the catalyst behaviour in the polymerization of dienes[4,8].

In this work the transition-metal compound was always added first in the form of a suspension in toluene, followed by either monomer or organoaluminium compound solution. In method A, monomer was added before the addition of organoaluminium compound and the order was reversed in method B. In *Table 1*, the variations of conversion and microstructure of polyisoprene are shown for different addition methods. It is quite evident that conversion was much affected by addition method but microstructure was less changed. Method A gave much more polyisoprene than method B for $Ce(acac)_3$ and $GdCl_3$ catalysts, while method B showed better conversion for $LuCl_3$ catalyst.

Ageing time

Addition method B was further complicated by the effect of catalyst ageing, so that the conversion and microstructure of polyisoprene for different ageing times were determined. As shown in *Figure 1*, the conversion decreased drastically for longer ageing times but the microstructure was unaffected in the case of $Ce(acac)_3$–DEAC catalyst system. The decrease in conversion might be due to the decomposition of active species with ageing time in the absence of monomer[4].

To avoid the effect of ageing on polymerization, method A was adopted for further study of catalyst behaviour.

Transition-metal compounds

It is well known that the transition-metal compounds have great effects on catalyst activity and stereoregularity for Ziegler–Natta polymerization[9]. The effects of various f-orbital transition-metal compounds on conversion and microstructure of polydienes were studied at constant monomer concentration, constant polymerization temperature and constant [DEAC]/[FTM], and the

Table 2 Effect of transition-metal compounds on conversion and microstructure of polydienes

	Isoprene						Butadiene				
Transition-metal compounds	Time (h)	Conversion (%)	Microstructure (%)				Time (h)	Conversion (%)	Microstructure (%)		
			Cis-1,4	*Trans*-1,4	3,4	1,2			*Cis*-1,4	*Trans*-1,4	1,2
$Ce(acac)_3$	5	93.7	0	94	6	0	3	4.4	–	–	–
$CeCl_3$	3	35.4	0	96	4	0	3	7.6	–	–	–
$GdCl_3$	5	101.8	0	93	7	0	5	9.6	29	70	1
$NdCl_3{\cdot}6H_2O$	3	72.4	0	91	8	1	3	6.0	32	65	3
$PrCl_3{\cdot}6H_2O$	3	50.1	0	94	5	1	3	7.2	22	69	9
$LuCl_3$	5	95.4	0	88	11	1	5	9.9	28	70	2
$UO_2(C_2H_3O_2)_2{\cdot}6H_2O$	3	74.0	0	93	6	1	3	22.3	–	–	–

[Dienes] $= 2.0 \pm 0.1$ mol l^{-1}, [FTM] $= (1.36 \pm 0.03) \times 10^{-3}$ mol l^{-1}, [DEAC]/[FTM] $= 20.0 \pm 0.5$; temperature 20°C

Table 3 Effects of organoaluminium compounds on conversion and microstructure of polyisoprene

	DEAC		TEA		TIBA	EADC	EASC
Transition-metal compounds	Conversion (%)	*Trans*-1,4 (%)	Conversion (%)	*Trans*-1,4 (%)	Conversion (%)	Conversion (%)	Conversion (%)
$Ce(acac)_3$	91.5	94	76.8	94	0	105.5	55.9
$PrCl_3{\cdot}6H_2O$	50.1	94	56.0	99	0	–	–
$UO_2(C_2H_3O_2)_2{\cdot}6H_2O$	74.0	93	33.0	100	0	–	–
None	–	–	–	–	–	100.7	30.0

[Isoprene] $= 2.0 \pm 0.1$ mol l^{-1}, [FTM] $= (1.36 + 0.03) \times 10^{-3}$ mol l^{-1}, [Al]/[FTM] $= 20.0 \pm 0.5$; temperature 20°C; time 3 h

Table 4 Effects of solvent on conversion and microstructure of polyisoprene

		Microstructure (%)			
Solvent	Conversion (%)	*Cis*-1,4	*Trans*-1,4	3,4	1,2
Toluene	93.7	0	94	6	0
Hexane	17.5	0	86	13	1

[Isoprene] $= 2.0 \pm 0.1$ mol l^{-1}, [$Ce(acac)_3$] $= (1.36 \pm 0.03) \times 10^{-3}$ mol l^{-1}, [DEAC]/[$Ce(acac)_3$] $= 20.0 \pm 0.5$; temperature 20°C; time 5 h

results are shown in *Table 2*. In the case of polyisoprene, the activity was relatively satisfactory and the microstructure of *trans*-1,4 was over 90% for various catalysts. Gd, Ce and Nd compounds showed higher activities, as reported by Chinese scientists, but the Lu compound gave a higher conversion, conflicting with Chinese results[10]. But these catalysts gave unexpectedly lower conversion and mixed microstructure for butadiene polymerization.

Organoaluminium compounds

Because the organoaluminium compounds also show dramatic effects on diene polymerization[9], the conversion and microstructure of polyisoprene were examined with various organoaluminium compounds and are shown in *Table 3*. As shown in *Table 3*, DEAC and TEA were found to be effective catalysts for isoprene polymerization while TIBA was not. Contrary to the previous report[3], the content of *trans*-1,4 structure was less changed with organoaluminium compounds.

Especially, it was found that isoprene could be polymerized with EADC or EASC alone in the absence of f-orbital transition-metal compounds and produced the cyclized polyisoprene[11], which was confirmed by i.r. study.

Solvent

To study the solvent effect on the $Ce(acac)_3$–DEAC catalyst system, the polymerization of isoprene was carried out in toluene or n-hexane and the results are shown in *Table 4*. The conversion was higher in toluene than in n-hexane, which is the reverse result compared to a previous one[3]. But the content of *trans*-1,4 structure was almost independent of solvent. The polymerization in toluene was more homogeneous in appearance because of the higher solubility of diene polymer in this solvent. In contrast, n-hexane gave a heterogeneous phase, and thus was a slurry process of polymerization.

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