Mechanism of Polymerization of Isoprene Catalyzed by Rhodium Complex—Allyl Alcohol—Sulfonic Acid System

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ABSTRACT: Isoprene is polymerized with a catalyst system consisting of a rhodium complex, allyl alcohol, and sodium dodecyl sulfate. The role of the emulsifiers was examined to elucidate the nature of the active species. Sodium dodecyl sulfate was found to be hydrolyzed even in a nonmicellar system to give sulfuric acid. Another experiment showed that isoprene was polymerized also by the catalyst system consisting of rhodium complex, allyl alcohol, and a strong acid such as toluenesulfonic acid, sulfuric acid, or nitric acid. From these results, it was assumed that an allyl ester of the strong acid was formed in the reaction system. The allyl ester presumably reacted with the rhodium complex to form a π -allyl complex, which was regarded as the active catalyst species in the isoprene polymerization. Allyl alcohol present in excess in the reaction system seemed to suppress cyclization reactions of the polymer formed.

KEY WORDS Mechanism of Polymerization / Sodium Dodecyl Sulfate / Rhodium Catalyst / Allyl Sulfonate / Emulsion Polymerization / Allyl Alcohol / Isoprene /

Butadiene has been known to undergo a stereospecific polymerization with rhodium catalysts in micellar systems of an alkyl sulfate or alkylbenzenesulfonate.¹ It was also reported that isoprene was not polymerized with rhodium nitrate in aqueous or nonaqueous media unless a sufficient amount of allyl alcohol ($[AlOH]/[Ip]=1$) was present in the reaction system.²

Several papers have dealt with the rhodium catalyzed polymerizations of butadiene and isoprene under various reaction conditions.³⁻⁸ None of them, however, seemed to elucidate the nature of the active catalyst species in the reaction system. To obtain a clearer picture of the active species of rhodium catalyst, a series of reactions of μ -dichloro-bis(π -cyclooctadiene-1, 5)-dirhodium (abbreviated hereafter as rhodium cyclooctadiene) with other components was studied in detail in aqueous and nonaqueous media.

EXPERIMENTAL

Materials

Solvents and reagents were purified by the usual methods,⁹ and all purification procedures were

carried out under nitrogen.

Isoprene was dried over Drierite, refluxed over calcium hydride, and then fractionally distilled under nitrogen. Allyl alcohol and ethyl alcohol were dried over Drierite and distilled fractionally. Methylene chloride was dried over Drierite, refluxed over calcium hydride, and then distilled fractionally. Chloroform was washed with sulfuric acid, water, aqueous sodium hydroxide, and water, in order. It was dried with calcium chloride, refluxed over calcium hydride, and distilled fractionally.

Rhodium Salt and Complex

Rhodium trichloride was used in the trihydrate form. μ -Dichloro-bis(π -cyclooctadiene-1, 5)-dirhodium, $[Rh(COD)Cl]_2$, was prepared according to Chatt.¹⁰ First, 1, 5-cyclooctadiene (20 ml) was added to a red solution of rhodium trichloride trihydrate (10 g) in ethanol (300 ml). Then the solution was refluxed with vigorous stirring for three hours. The reaction mixture was allowed to stand at room temperature to precipitate yellow crystals of rhodium cyclooctadiene, which were purified by reprecipitation from methylene chloride

with cyclohexane. All procedures were carried out under a nitrogen atmosphere.

Anal. Calcd for $[\text{Rh}(\text{C}_8\text{H}_{12}\text{Cl})_2]$: C, 38.97; H, 4.91.

Found: C, 39.08; H, 5.08.

Sodium Dodecyl Sulfate

Sodium dodecyl sulfate provided by Kao Soap Co. was purified with ethanol.

Allyl p-Toluenesulfonate

Allyl *p*-toluenesulfonate was prepared according to Stoll.¹¹ Finely powdered silver carbonate (20 g) was added by portions with stirring to a hot (90°C) water solution (400 ml) of *p*-toluenesulfonic acid (27 g) in a 1-l beaker. After the complete evolution of the carbon dioxide gas, the hot water solution was filtered. Evaporation of the water left a white residue of silver *p*-toluenesulfonate. The white powdered crystal of silver *p*-toluenesulfonate was added to allyl bromide (35 ml) in benzene (150 ml), and refluxed for 30 min. The hot reaction mixture was filtered. The filtrate was evaporated, leaving an oily residue containing allyl *p*-toluenesulfonate. An ethereal solution (200 ml) of the residue was washed with water (100 ml) three times, and was dried over magnesium sulfate. A viscous liquid of allyl *p*-toluenesulfonate was obtained after evaporation of ether, and was purified by column chromatography (benzene—silica gel; diameter, 30 mm; *l*, 250 mm); yield, 33%.

Polymerization of Isoprene and Purification of Polyisoprene

Polymerization of isoprene and purification of polyisoprene were carried out in the same way as reported in a previous paper.¹³ Methylene chloride was used as the solvent for the rhodium cyclooctadiene.

Determination of Microstructures of Polyisoprene

Microstructures were determined according to the method described in a previous paper.¹³

RESULTS AND DISCUSSION

The Role of Sodium Dodecyl Sulfate as a Component of the Rhodium Catalyst System

It was reported in a previous paper¹³ that rhodium complex, allyl alcohol, and sodium dodecyl sulfate were the indispensable components for the isoprene polymerization. This result suggested that a reaction product between sodium dodecyl

sulfate and allyl alcohol might be responsible for the formation of active catalyst species from the rhodium complex. Since the samples of polyisoprene formed in the reaction systems, (1) and (2), were found to have much the same microstructure (*cis*-1, 4 55%; *trans*-1, 4 38%; 3, 4 7%), it was considered that the active species in the two systems should probably have essentially the same nature. Homogeneous nonaqueous system:

Aqueous emulsion system:

where Ip, AlloH, and SDS denote isoprene, allyl alcohol, and sodium dodecyl sulfate, respectively.

To elucidate the mechanism of formation of the active species, examinations were carried out with respect to the individual reagent involved in the reaction system. In the first step, sodium dodecyl sulfate, which was insoluble in methylene chloride, was mixed with the solution of rhodium cyclooctadiene in methylene chloride (system (3)). After heating the system (3) at 65°C for 72 hr, the formation of sodium sulfate and *n*-dodecyl alcohol was detected in the reaction system. The hydrolysis reaction was caused by a small amount of water contained in the sodium dodecyl sulfate sample. No hydrolysis of the sodium dodecyl sulfate, of course, took place when the sample of sodium dodecyl sulfate was used after being dried under vacuum at 65°C.

More than 95% of the rhodium cyclooctadiene was found to be unchanged in terms of the NMR analysis. The hydrolysis reaction of sodium dodecyl sulfate, however, seemed to have a correlation with the amount of rhodium cyclooctadiene present in the system, as shown in Figure 1. It may be suggested from these results that a weak coordination of the sulfate group to the rhodium cyclooctadiene results in the activation of sodium dodecyl sulfate, which makes the latter compound more susceptible to the hydrolysis reaction.

Figure 1. Hydrolysis of sodium dodecyl sulfate in reaction system (6): (a), calculated from feed reagents; (b), the value of $[n\text{-C}_{12}\text{H}_{25}\text{OH}] / [\text{COD}]$ determined by $^1\text{H-NMR}$.

In this system, the water formed by redox reactions of allyl alcohol was probably used in the hydrolysis reaction of sodium dodecyl sulfate in system (4). The direct hydrolysis product, sodium bisulfate, was known to be disproportionated into sodium sulfate and sulfuric acid under the reaction conditions.¹³

Table I. Isoprene polymerization with rhodium complex

Run	Emulsifier or strong acid	Solvent	Temp, °C	Yield, ^a %	Microstructure of polyisoprene, %		
					cis	trans	3,4
1	$n\text{-C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	$\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ (15 ml)	20	91	56	37	7
2	"	"	65	99	55	38	7
3	"	CH_2Cl_2	20	5	58	33	9
4	"	"	65	72	59	34	7
5	$\text{CH}_3\text{SO}_3\text{Na}$	$\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ (15 ml)	65	14	46	49	5
6	"	CH_2Cl_2	65	81	46	48	6
7	[filtrate of system (6)]	CH_2Cl_2	20	47	61	29	10
8	[after heating]	"	65	79	46	47	7
9	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	CH_2Cl_2	20	98	59	32	9
10	"	"	20	13	?	?	?
11	H_2SO_4	$\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ (5 ml)	65	20	50	44	6
12	HNO_3	CH_2Cl_2	50	5	65	27	8
13	HCl	"	50	0	—	—	—

^a MeOH insoluble part of polyisoprene formed.

Reaction conditions: $[\text{Rh}(\text{COD})\text{Cl}]_2$, 75 mg; CH_2Cl_2 , 5 ml; isoprene, 2.5 ml; allyl alcohol, 1.7 ml, 0.035 ml (run 10); emulsifier or strong acid, 1.2 mmol, 3 mmol (run 13); reaction time, 72 hr, 13 hr (run 13).

* See eq 3. ** See eq 5.

The emulsifier, sodium dodecyl sulfate, was thus proven to play an important role as the source of sulfuric acid in the polymerization system.

Comparison of the Polymerization Behaviors in Aqueous and Nonaqueous Systems

A series of experiments was carried out to find the characteristic features associated with the aqueous polymerization system in comparison with the nonaqueous one. Results are shown in Table I.

In micellar systems with sodium dodecyl sulfate, polyisoprene was obtained in high yields (91% and 99%, respectively) both at 20°C and 65°C. A fairly high yield (72%) of polyisoprene was also obtained in nonaqueous systems with sodium dodecyl sulfate at 65°C, while only a low yield (5%) of the polymer was obtained at 20°C. Sodium methyl sulfate, in contrast with sodium dodecyl sulfate, polymerized isoprene in an aqueous system in low yield (14%) at 65°C, while in a nonaqueous system in high yield (81%) at 65°C (Table I-5, 6). These results suggest that the micellar system is not the crucial condition for the rhodium catalyzed polymerization of isoprene. A high yield of polyisoprene was obtained from the reaction system (6) where a filtrate of system (3) was used after heating it at 65°C for 72 hr.

(filtrate of system (3) after heating)
(5 ml)

It is evident that sulfuric acid released from sodium dodecyl sulfate by hydrolysis was involved in the filtrate. As reported previously,¹³ a catalyst system having toluene-sulfonic acid instead of sulfuric acid also induced the polymerization of isoprene in a nonaqueous system (reaction (7), Table I-9) to give the polymer in high yield.

Nitric acid exhibited a cocatalytic effect on the rhodium catalyzed isoprene polymerization, but hydrochloric acid did not (Table I-11-13). These results are consistent with the reported fact that

Figure 2. Conversions of isoprene and allyl alcohol as a function of time in reaction (10): ○, isoprene; △, allyl alcohol.

rhodium nitrate was active as a catalyst in isoprene polymerization, in contrast with rhodium chloride.²

The conversions of isoprene and allyl alcohol as a function of time were measured at 20°C in system (8) (Figure 2).

The rate of consumption of isoprene monomer in system (8) was found to depend on the first order with respect to the concentration of isoprene. The consumption of allyl alcohol was very small.

Isoprene Polymerization with the Allyl Sulfonate—Rhodium Complex System

A possible formation of allyl sulfate or sulfonate was suggested from the result that the presence of a strong acid together with allyl alcohol was essential for the isoprene polymerization catalyzed with rhodium complex (see section 2). The ability of allyl toluenesulfonate to participate in the formation of active species of catalyst was examined. Reactions of allyl toluenesulfonate with rhodium cyclooctadiene complex were carried out in comparison with those of propyl toluenesulfonate. ¹H-NMR measurements showed that the allyl ester reacted smoothly with the rhodium complex, while propyl ester did not. After an appropriate procedure, shown in (9), multiplet peaks (δ 4.6-4.9) were observed in the ¹H-NMR spectrum;

these were assigned to the methine proton of π -allyl group (Figure 3).

A catalyst system consisting of allyl toluenesulfonate and rhodium cyclooctadiene complex polymerized isoprene; a methanol insoluble part of the polyisoprene was obtained in 47-% yield, [system (10)]. The ^1H -NMR spectrum of the polymer is shown in Figure 4.

Figure 3. NMR spectra of system (9) before and after the reaction.

The polyisoprene sample obtained from the non-aqueous system (10) was found by ^1H -NMR to have a cyclized structure. A rather high concentration of strong acid ester or its decomposition products in the reaction system might induce cyclization of linear polyisoprene, which was formed in a way similar to the standard recipe such as (1).

When the same polymerization reaction as in (10) was carried out in the presence of excess allyl alcohol, polyisoprene having the normal micro-

Figure 4. NMR spectrum of polyisoprene obtained from reaction system (10).

structure was produced, as shown in Table II-5. It is considered, therefore, that allyl alcohol in excess in the reaction system would prevent the cyclization of polyisoprene by interacting with a cationic species to decrease its reactivity.

Polymer yields in isoprene polymerizations with the catalyst systems containing toluenesulfonic acid or esters and allyl alcohol were compared. The results obtained are shown in Table II.

At 65°C , polymer yields were very high in all runs. At 20°C , on the other hand, propyl toluenesulfonate exhibited no activity, in contrast with the high activity of allyl toluenesulfonate. Dimethyl sulfate and toluenesulfonic acid also showed high activity. This temperature effect may be explained in terms of the ease of formation of allyl sulfate or sulfonate in the reaction systems.

The allyl ester, however, was not detectable by ^1H -NMR nor by ^{13}C -NMR after mixing toluene-

Table II. Effects of toluenesulfonic acid and esters on isoprene polymerization with rhodium catalyst

Run	Acid or ester	Temp, °C	Yield, ^a %	Microstructure of polyisoprene, %		
				<i>cis</i>	<i>trans</i>	3, 4
1	CH ₃ -C ₆ H ₄ -SO ₃ H	20	98	59	32	9
2	"	50	90	50	44	6
3	CH ₃ -C ₆ H ₄ -SO ₃ C ₃ H ₇	20	0	—	—	—
4	"	65	41	—	—	—
5	CH ₃ -C ₆ H ₄ -SO ₃ CH ₂ CH=CH ₂	20	100 ^b	66	—	—
6	(CH ₃) ₂ SO ₄	20	58	62	27	11
7	"	65	99	46	46	8

^a Methanol insoluble part of polyisoprene.^b Determined by NMR analysis of the reaction mixture.Reaction conditions: [Rh(COD)Cl]₂, 75 mg; isoprene, 2.5 ml; allyl alcohol, 1.7 ml; acid or ester, 1.2 mmol; reaction time, 72 hr.

sulfonic acid with allyl alcohol in the absence of the rhodium complex in methylene chloride. When the concentration of allyl alcohol in the system was not high enough, the yield of polyisoprene was very low (see Table I-10). It was assumed that the equilibrium (11) would shift very much to the left side. The allyl toluenesulfonate formed might have reacted with the rhodium complex immediately after it was formed in the system.

Mechanism of Isoprene Polymerization with Rhodium Complex in Emulsion System

The mechanism of isoprene polymerization with rhodium complex in an emulsion system can be discussed in the light of the results described in the preceding sections. In the first step, sodium alkyl sulfate is hydrolyzed to some extent to give sulfuric acid. The sulfuric acid formed will be converted to its allyl ester as an intermediate. The latter reacts with the rhodium cyclooctadiene complex to form π -allyl species. These reactions are considered to take place in a hydrophobic zone which is constructed by the emulsifier.

In the emulsion polymerization of butadiene

catalyzed by rhodium chloride, it was reported⁴ previously that crotonaldehyde was formed in the polymerization system. Presumably, crotonaldehyde was formed by the oxidation of crotyl alcohol, which was an addition product of water to butadiene. It is to be noted that the butadiene polymerization could take place without the aid of allyl alcohol, which forms a sharp contrast with the isoprene polymerization. Crotyl alcohol in the butadiene polymerization must have played a similar role to allyl alcohol in the isoprene polymerization.

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