Polymerization of Isoprene with a Tin Tetraalkyl-Titanium Tetrachloride Catalyst

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Many studies[1,2] of the polymerization of isoprene have been undertaken in an attempt to prepare a natural rubber-like polymer using such a typical Ziegler catalyst as aluminum trialkyl-titanium tetrachloride. Moreover, Saltman et al.[3] studied the mechanism of isoprene polymerization with aluminum triisobutyl-titanium tetrachloride.

There is a patent[4] concerning isoprene polymerization using tin tetraalkyl as a component of the catalyst system of SnR_4-$TiCl_4$-$AlCl_3$. However, the catalyst system is so complicated that any analysis of the reaction scheme is comparatively difficult. The authors, therefore, studied the polymerization by a comparatively simple catalyst system consisting of two components, tin tetraalkyl and titanium tetrachloride, in order to obtain fundamental data prior to treating a more complicated system.

Experimental

Materials. — Isoprene was synthesized by the thermal decomposition of limonene according to Staudinger's method[5] and was purified by redistillation. Commercial solvents such as *n*-hexane, benzene and toluene were purified by distillation after drying them with sodium. Titanium tetrachloride was treated with copper dust and distilled. Tin tetraalkyl was synthesized by the usual method[6], i. e., by the reaction between a Grignard reagent and tin tetrachloride in ether, and was employed after a by-product, R_3SnCl, had been removed.

Polymerization. — In every case, the catalyst complex was prepared by mixing the two components at room temperature in a polymerization tube filled with gaseous nitrogen. Then the complex was aged at that temperature for about 30 min., except for the case of finding the effect of the aging time on the polymerization rate. The complex thus produced was usually a large block. After a solvent, benzene or hexane, had been poured into the tube, the block was divided as finely as possible by high speed shaking. Then the tube was cooled in dry ice-methanol and sealed after a desired amount of monomer had been introduced into it. The reaction was started by transferring the tube into a constant temperature bath. The polymer produced was dipped in methanol containing hydrochloric acid to decompose the catalyst residue, filtered, washed thoroughly with methanol, and dried.

Investigation of Microstructure. — The microstructure of the polymer was investigated by infrared-measurement of the absorption bands in the $750\sim900\ \mathrm{cm}^{-1}$ region. The sample was placed between two rock salt plates to protect it from oxidation during the measurement. This protective procedure was found to be necessary, particularly in the case of measurements at elevated temperatures.

Measurement of Viscosity. — The Viscosity of the soluble part of the polymer was measured in toluene as a solvent at 30°C. Thus, the intrinsic viscosity was obtained.

Results

Effect of the Aging Time on the Polymerization Rate.—The relation between the aging time and conversion is shown in Fig. 1. In this case, the polymerization was carried out with a tin tetraethyl-titanium tetrachloride catalyst at 25°C for one hour. The Sn/Ti ratios shown by the A, B and C lines were 1.40, 2.25 and 0.28 respectively. The polymerization rate dropped suddenly in the initial stage and became almost constant after

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[1] E. g., H. E. Adams, R. Stearns, W. A. Smith and J. L. Binder, *Ind. Eng. Chem.*, **50**, 1507 (1958).

[2] N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers", Interscience Publishers, Inc., New York (1959), p. 372.

[3] W. M. Saltman, W. E. Gibbs and J. Lal, *J. Am. Chem. Soc.*, **80**, 5615 (1958).

[4] Solvay and Cie., Belg. Pat. 547618 (1956).

[5] H. Staudinger and H. W. Klever, *Ber.*, **44**, 2212 (1911).

[6] P. Pfeiffer and K. Schnurmann, ibid., **37**, 319 (1904).

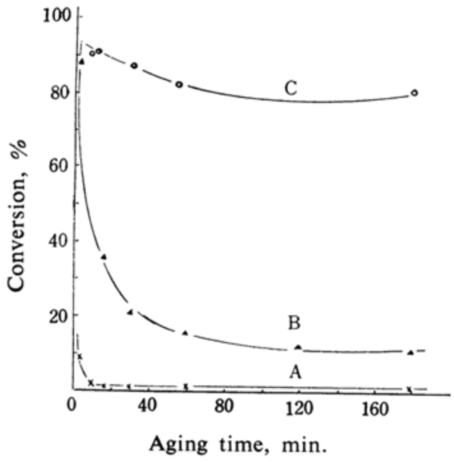

Fig. 1. Effect of aging time on the polymerization rate. Catalyst composition (Sn/Ti) ;
A : 1.40, B : 2.25, C : 0.28
$TiCl_4$, 5.46×10^{-3} mol.; monomer, 5 cc.; hexane, 5 cc.

a certain aging time although the time required for this constancy to be attained was different according to the variation in the molar ratio of the catalyst components.

Effect of Catalyst Composition on the Properties of the Polymer.—Here, properties of polymer' indicates the solubility, the intrinsic viscosity and the microstructure. The experiments for investigating these properties were performed on the polymers produced by the $Sn(i\text{-}C_3H_7)_4$-$TiCl_4$ catalyst at 40°C. In this case, the amount of monomer used was 10 cc. in each polymerization. The polymer was extracted by boiling toluene after being purified. Solubility and intrinsic viscosity are summarized in Table I.

TABLE I. POLYISOPRENE PRODUCED BY $Sn(i\text{-}C_3H_7)_4$-$TiCl_4$

No.	SnR_4 $\times 10^2$ mol.	Sn/Ti	Soluble part %	$[\eta] \times 10^2$
1	0.203	0.22	71.0	5.64
2	0.406	0.44	90.8	5.68
3	0.812	0.88	75.4	4.88
4	1.218	1.31	73.3	4.57
5	1.624	1.75	81.3	5.30

$TiCl_4$, 9.26×10^{-3} mol.; monomer, 10 cc.; benzene, 10 cc.; temp., 40°C, time, 4 hr.

From the table it can be concluded that the yield of a soluble part and the intrinsic viscosity have no direct connection with the catalyst composition. Generally, the molecular weight (deduced from the intrinsic viscosity) of polyisoprene produced by the SnR_4-$TiCl_4$ catalyst seems to be low.

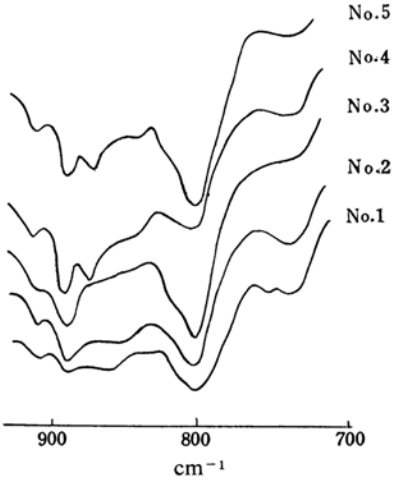

Fig. 2. Infrared spectra of the samples produced by $Sn(i\text{-}C_3H_7)_4$-$TiCl_4$.

Microstructure.—The infrared spectra of the samples shown in Table I are represented in Fig. 2. The spectra indicate that the microstructure of the polymers is similar to that of gattapercha, shown in Fig. 3. Therefore, it is clear that the polymers consist for the most part of *trans*-1, 4 structure.

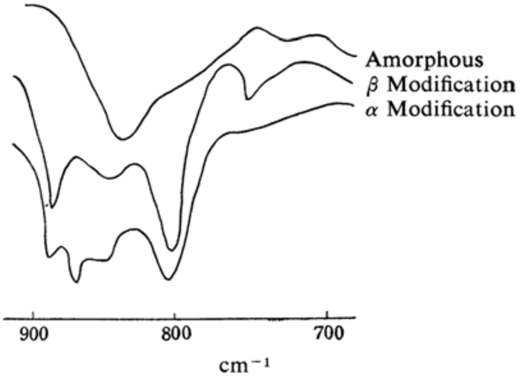

Fig. 3. Infrared spectra of guttapercha, cited from Richardson's paper⁷⁾.

Later some of the absorption bands which appeared in 750∼900 cm^{-1} region will be discussed. Here, let it only be noticed that the microstructure is greatly affected by the catalyst composition. When the tin tetraalkyl increased to some extent, the microstructure had a close resemblance to that of the α type of guttapercha.

Crystalline Band.—The infrared spectra of the sample of No. 5 were observed in a molten and annealed state (Fig. 4). The specimen was treated carefully to prevent it from oxidation. Figure 4 shows the results obtained

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7) W. S. Richardson and A. Sacher, *J. Polymer Sci.*, **14**, 353 (1953).

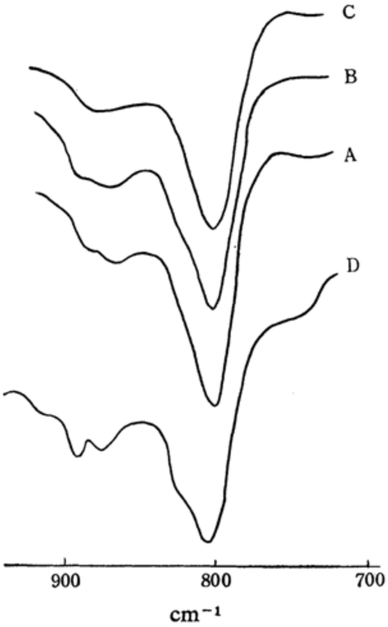

Fig. 4. Infrared spectra of No. 5 at various temperatures.
A: 85°C, B: 105°C, C: 150°C, D: annealed.

at 85, 105 and 150°C and in the annealed state. Since the intensity of the bands at 870 and 890 cm^{-1} decreased with an increase in the temperature and since they reappeared in the re-cooled state, it may be said that they resulted from the crystalline structure.

Here, it must be noted that the crystalline band does not reappear, even if the polymer is crystallizable, when the observation is made as soon as the specimen is re-cooled. The facts was confirmed by a preliminary experiment using a crystalline guttapercha.

Simple Kinetics.—The effects of monomer and catalyst concentration on the polymerization rate were investigated using the $SnEt_4$-$TiCl_4$ catalyst, in which the Sn/Ti ratio is constant (1.09). Tables II and III show the results obtained from the polymerization with a constant concentration of monomers and a constant concentration of catalysts respectively. The tables show that the over-all reaction rate is of the first order with respect to the concentration of the catalysts and monomers, [C] and [M].

$$R_p = k[C][M]$$

Here, [C] means the concentration of titanium tetrachloride.

TABLE II. POLYMERIZATION UNDER CONSTANT CONCENTRATION OF MONOMER

[C] (mol./l.) ×10	R_p (mol./l./sec.) × 10^5
0.618	1.88
1.853	3.20
3.705	5.35
6.176	8.38

Monomer, 5 cc.; hexane, 10 cc.; Sn/Ti, 1.09

TABLE III. POLYMERIZATIONS UNDER CONSTANT CONCENTRATION OF CATALYST

Monomer cc.	*n*-Hexane cc.	R_p (mol./l./sec.) × 10^5
5	25	4.81
15	15	13.1
20	10	18.1

$SnEt_4$, 10.12×10^{-3} mol.; $TiCl_4$, 9.26×10^{-3} mol.; temp., 21°C

Over-all Energy of Activation. — In all experiments at various temperatures, 0.1 mol. of monomer was polymerized in 5 cc. of an *n*-hexane solution containing 10.12×10^{-3} mol. of tin tetraethyl and 9.26×10^{-3} mol. of titanium tetrachloride. The results are represented in Fig. 5. By plotting the R_p calculated from Fig. 5 against $1/T$, Fig. 6 was obtained. Therefore, the value of the apparent activation energy was obtained as 13.6 kcal./mol.

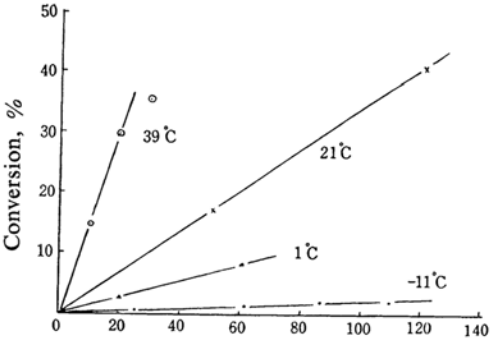

Fig. 5. Polymerization rates at various temperatures.

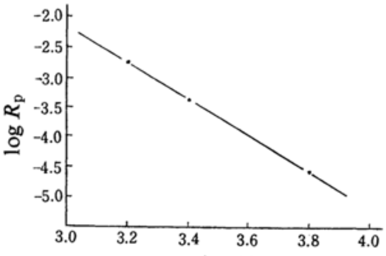

Fig. 6. Relation between log R_p and $1/T$.

Discussion

From the reaction of SnR_4 and $TiCl_4$, such reaction products as R_3SnCl, R_2SnCl_2, etc., and

$RTiCl_3$, R_2TiCl_2, etc., can be expected. However, any one product may have little or no catalytic activity, so that the true catalyst causing the polymerization to start might be a complex the form of which is not clear.

As we[8] discussed previously in connection with the polymerization of propylene with the same catalyst, the catalyst system has a cationic or an anionic character according to the existence of either $TiCl_4$ or SnR_4 in excess.

Since the polymerization rate is of the first order with respect to the concentration of the catalysts, the reaction mechanism can be considered to be a typical ionic type-probably a coordinated anionic type. It was also considered that termination will occur as a result of the abstraction of the hydrogen from the solvent or from other materials.

The comparatively small value of the activation energy is also in good agreement with a concept of an ionic mechanism. The value is slightly smaller than that (14.4 kcal./mol.) obtained by Saltmann, who used an aluminum triisobutyl titanium tetrachloride catalyst.

It must be noted that when SnR_4 is used as a catalyst component, the charactor of the complex depends not only on the catalyst composition but also on the aging time, because the reaction between SnR_4 and $TiCl_4$ is rather slower than the reaction between AlR_3 and $TiCl_4$. As is well known, the reaction of the latter combination is so violent that the complex is produced as soon as the two components are mixed. In the case of the former combination, so long as the reaction of the components is incomplete, free titanium tetrachloride remains in the catalyst system. which gives rise to a comparatively rapid polymerization. Figure 1 clearly shows the relationships. The abrupt drop in the polymerization rate which appeared at the initial stage of reaction (hence, a shorter aging time), means a decrease in the free titanium tetrachloride and an increase in the catalyst complex.

The reason why the catalytic activity of C is the highest will be due to the somewhat cationic character of the catalyst system because of excess titanium tetrachloride. The other lines, A and B, represent anionic polymerization except for the initial stage, because tin tetraalkyl was used in excess. The fact that the B line is higher than the A line may be attributed to the existence of more effective complexes in the former than in the latter.

We will now discuss the results shown in Fig. 2. The following descriptions concerning the assignment of various absorption bands are based on Richardson's paper[7]. Absorption bands are present at 750, 800 and 909 cm^{-1} in every polymer (Nos. 1—5); the bands represent β modification, a crystalline type of *trans*-1,4 structure, or a *cis*-1,4, *trans*-1,4 and 1,2 structure respectively.

Other specific bands in the polymers of Nos. 4 and 5 (the first group) exist at 870 and 890 cm^{-1}; the former band is attributed to α modification and the latter to both α- and β modification. Comparing the two bands, the latter is relatively more intense than the former, and hence the polymer in the first group can be considered to be a mixture of the two modifications. The variation in crystalline type between α and β is affected by the temperature, so that both types may exist as a mixture at a suitable temperature.

A specific band in the other polymers (Nos. 1—3, the second group), at 887 cm^{-1}, is attributed to the 3,4 structure. If the polymer were an example of β modification, a specific band for the type would be present at 890 cm^{-1}. Therefore, the band at 750 cm^{-1} mentioned above may be due to the *cis*-1,4 structure. After all, it is not clear from the infrared study whether or not the crystallinity is present in the polymers of the second group.

Further investigation concerning the spectra is being undertaken from the viewpoint of catalyst composition. The polymers in the first group are produced by the complex where the Sn/Ti ratio is larger than unity, while those in the second group are produced under the reverse conditions. Accordingly, it may be said that a complex having an anionic character produces a crystalline polymer, exemplifying α- and β-modification of *trans*- 1,4-polyisoprene, and that that having a cationic character produces a polymer consisting of various structures.

In addition to the infrared study, we examined the X-ray diffraction pattern of the sample, which had been considered a crystalline polymer as a result of the infrared study, but we could not obtain the crystalline pattern. This may be because the crystallite contained in the polymer is too small to represent the crystalline X-ray pattern, while it is large enough to represent the crystallinity in infrared measurement.

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[8] N. Ashikari and M. Honda, This Bulletin, 34, 767 (1961).