[CONTRIBUTION FROM RESEARCH LABORATORY, CELANESE CORPORATION OF AMERICA]

Polymerization of Hexene-1 with Titanium Tetrachloride–Aluminum Triisobutyl

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An investigation has been made of the polymerization of hexene-1, using titanium tetrachloride–aluminum triisobutyl, at atmospheric pressure and at 10–50°. Polyhexenes formed had low molecular weight and were low melting. The polymerization rate is first order with respect to the monomer concentration. The apparent activation energy at a catalyst ratio ($TiCl_4$:$Al(i\text{-}C_4H_9)_3$) of 2:1, based on measurements of initial rates, has been found to be 9.5 kcal. per mole. Inhibition experiments with triethylamine showed that the reaction could be stopped, maintained in a dormant state, and then restarted by addition of fresh catalyst.

As an extension of the investigation previously reported for ethylene polymerization,[1] this paper contains a summary of some results on the polymerization of hexene-1 using the same catalyst system. No data on the polymerization of hexene-1, using the titanium tetrachloride–aluminum triisobutyl catalyst, have been reported previously other than the observation by Reding[2] that the polymer formed has a very low melting point which is at the minimum for the series of normal poly-α-olefins.

Experimental

Experiments were carried out in an apparatus similar to that previously described.[1] The solvent (sodium-dried, distilled cyclohexane) in an amount so as to make the total volume (including catalyst and monomer which were added later) of the reaction mixture 400 ml., was added to the dry reaction flask. Temperatures were maintained constant by water or ice-water baths to ± 0.5°. Catalyst addition was then made in the manner previously described.[1]

Immediately after addition of the two catalyst materials, hexene-1 monomer was pipetted into the reaction flask. Hexene-1 used (Matheson, Coleman and Bell) had boiling point 63–64° and refractive index $n^{25}\text{D}$ 1.3870.

Throughout the experiment the rate of polymerization was followed by pipetting out 3-ml. samples at definite time intervals. The sample was added to 10 ml. of water in a glass-stoppered flask and cooled in an ice-bath prior to titration for unsaturation. The bromide–bromate method[3] for olefin titration was used. Thirty milliliters of 0.200 *N* bromide–bromate solution were added to the flask followed by 10 ml. of 6 *N* sulfuric acid. The stoppered sample was allowed to remain in the dark for 20 minutes after which time 15 ml. of 10% potassium iodide was added and iodine titrated with 0.100 *N* sodium thiosulfate (starch indicator). Reproducible results (within *ca.* 2%) were obtained by this method. Titration of the starting material (hexene-1) in cyclohexane solution agreed very well with the expected value.

Throughout each experiment the mixture was maintained in a nitrogen atmosphere by allowing a slow stream (*ca.* 200 ml. per min.) of nitrogen to enter the reaction flask through a gas inlet tube above the surface of the reaction mixture. The experiments were found to be reproducible.

At the end of each experiment 200 ml. of methanol containing 3% concentrated hydrochloric acid were added directly to the reaction flask. A small amount of water was then added, the cyclohexane layer separated and the aqueous layer extracted with cyclohexane. The cyclohexane solution was water washed and dried over calcium chloride. Evaporation of the dried cyclohexane solution yielded the polymer.

A rough estimate of the melting points of the polymers formed was obtained by placing the liquid polymer in a tube and freezing in a carbon dioxide–acetone or liquid nitrogen bath. After removal of the frozen polymer from the cooling bath, it was allowed to warm. The melting point was then measured.

Unsaturation in the polymer was determined by direct titration (bromide–bromate method).

Results and Discussion

The nature and properties of the polymer formed was found to be strongly dependent on the catalyst ratio (titanium tetrachloride: aluminum triisobutyl). Using a catalyst ratio of 2:1 the polymer formed was liquid at room temperature with a low melting point (approximately −70°). A change in the catalyst ratio to 1:3 led to formation of a viscous translucent gum whose melting point was somewhat higher (approximately −30°). The melting point recorded by Reding[2] for the polymer formed (with an unspecified catalyst ratio) using this catalyst system is −55°.

Polyhexenes formed are unsaturated, the amount of unsaturation decreasing in changing from a catalyst ratio of 2:1 to 1:3. A summary of some experiments showing these observations is given in Table I. It should be noted that variation in properties of the polymer formed by variation of the catalyst ratio has been noted previously for ethylene polymerization.[1] In the case of ethylene,

TABLE I

HEXENE-1 POLYMERIZATION

(Solvent, cyclohexane: reaction mixture volume, 400 ml.; reaction time, 120 min.)

	Catalyst				Polymer formed			
Expt. no.	$TiCl_4$ (m-mole)	$Al(i\text{-}C_4H_9)_3$ (m-mole)	Reaction temp. (°C.)	Hexene-1 (g.)	Wt. (g.)	Unsat. (meq./g.)	M.p. (°C.)	Mol. wt.[a]
			Liquid polymer formation					
1	20	10	10	16.8	9.9	4.12	−66	423
2	20	10	30	16.8	11.6	4.19	−74	445
3	20	10	50	16.8	13.0	4.05	−78	434
4	20	10	30	5.4	2.9	2.40		
5	20	10	30	8.8	5.4	3.56		
6	20	10	30	16.8	11.6	4.19		
7	20	10	30	16.8	10.0		−74	
8	20	10	30	22.9	14.3	4.05		
9	10	5	30	16.8				
2	20	10	30	16.8	11.6	4.19		
10	40	20	30	16.8	13.0			
11[b]	20	10	30	16.8	11.4	3.20		
			Viscous translucent gum polymer formation					
12	8	24	30	8.8	2.1			
13	8	24	30	16.8	8.9	1.59	−26	
14	7.5	22.5	30	16.8	5.8		−28	

[a] By freezing point depression (solvent, cyclohexane).
[b] In this experiment 2 mmoles of inhibitor (triethylamine) was added after 12.5 min. After 24 min. in the inhibited state, fresh catalyst (20 mmole $TiCl_4$, 10 mmole TIA) was added.

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[1] E. J. Badin, THIS JOURNAL, **80**, 6545 (1958).

[2] F. P. Reding, *J. Poly. Sci.*, 547 (1956).

[3] J. Mitchell, I. M. Kolthoff, E. S. Proskaner and A. Weissberger, "Organic Analysis," Vol. III, Interscience Publishing Co., New York, N. Y., 1956, pp. 246–253.

TABLE II

RATES OF HEXENE-1 POLYMERIZATION

(Solvent, cyclohexane; reaction mixture volume, 400 ml.; reaction time, 120 min.)

Expt. no.	Catalyst $TiCl_4$ (mmole)	Catalyst $Al(i\text{-}C_4H_9)_3$ (mmole)	Reaction temp. (°C.)	Initial hexene-1 concn. (mole/l.)	Initial rate (mole/l./sec.)	Time (min.) for given fraction of monomer to react 0.10	0.25	0.50
1	20	10	10	0.50	0.00014	5	14	35
2	20	10	30	.50	.00045	2	6	18
7	20	10	30	.50	.00038	..	..	..
3	20	10	50	.50	.00061	1	3	10
15	20	10	50	.50	.00066	..	..	..
4	20	10	30	.16	.0001	3	11	33
5	20	10	30	.26	.0002	3	7	23
7	20	10	30	.50	.0004	2	6	18
8	20	10	30	.68	.0003	4	10	28
9	10	5	30	.50	.0001	4	13	..
2	20	10	30	.50	.0004	2	6	18
10	40	20	30	.50	.0006	1	2	5
16	60	30	30	.50	.0012	0.5	1	3

changes of molecular weight, melting point and structure (as shown by infrared) result when the catalyst ratio is altered.

Molecular weights of polyhexenes were in all cases lower than polyethylenes resulting from similar experiments. If one makes the assumption that there is one double bond per polymer molecule, the molecular weights of the liquid polymers are fixed in the region of about 400. In one case distillation of a polymer (experiment 2, Table I) showed the boiling range

20%	106–130° (2.5 mm.)
16%	131–155° (2.5 mm.)
34%	149–196° (0.7 mm.)
30%	Higher boiling residue

This also places the molecular weight in the same low region. Molecular weights by freezing point depression in cyclohexane (Table I) agree well with estimates from unsaturation. The semi-solid polymers formed with catalyst ratios of 1:3 were not distillable and seemed to be of higher molecular weight. An estimate from unsaturation would place the molecular weight in the region of 1000.

Some kinetic data have been collected and are shown in Table II and in Fig. 1 and 2. The rate constants for initial rates of reaction based on the initial slopes of experiments as in Figs. 1 and 2 have been listed in Table II. In addition, times necessary for fractions of 0.10, 0.25 and 0.50 of the monomer to have reacted are recorded. Results in the second set (experiments 4, 5, 7 and 8) of data in Table II based on Fig. 1, show that these values for tenth-life, quarter-life and half-life are essentially constant. Average values for these three times in this set of data are 3, 8 and 26 minutes. This approximate constancy indicates the reaction is first order with respect to the monomer.

Variation of the rate of reaction with temperature is shown by the first set of data in Table II and in Fig. 2. Quantitative estimate of the apparent activation energy based on the temperature range 10 to 30° leads to a value of 9.5 kcal. per mole. Extension of the data to a wider temperature range and different catalyst ratios led, as in the case of ethylene,[1] to deviations in the apparent activation energy. Such peculiar behavior has been tentatively ascribed to variations in the nature of the catalyst surface.

The precise nature of the reaction is still in doubt.

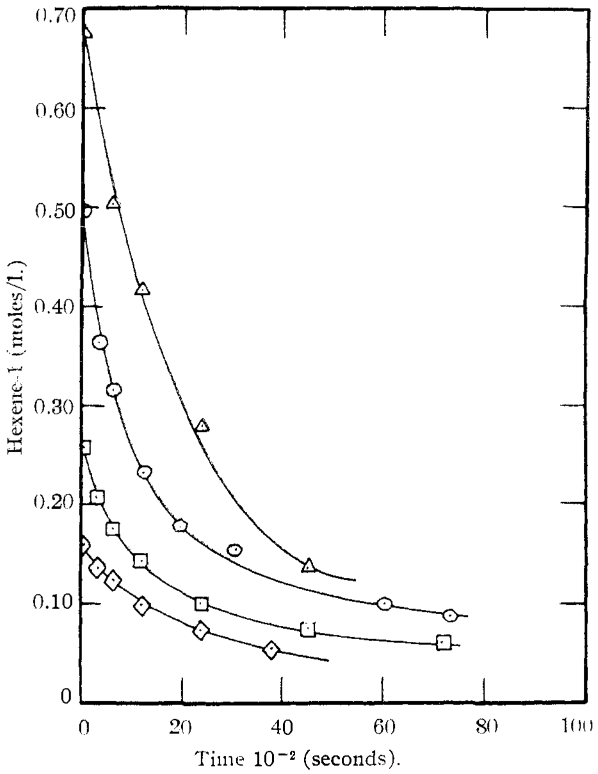

Fig. 1.—Hexene-1 polymerization at 30°. Variation of rate of polymerization with initial monomer concentration; (catalyst, 20 mmoles $TiCl_4$, 10 mmoles $Al(i\text{-}C_4H_9)_3$; solvent, cyclohexane).

The reactions involved in catalyst formation are probably

$$TiCl_4 + AlR_3 \longrightarrow RTiCl_3 + AlR_2Cl \quad (1)$$

$$RTiCl_3 \longrightarrow R + TiCl_3 \quad (2)$$

Dissociation of the transiently formed $RTiCl_3$, in association with other molecules, can then conceivably lead to initiation and propagation of the reaction. It may be pointed out here that infrared examination of the polyhexenes showed a more

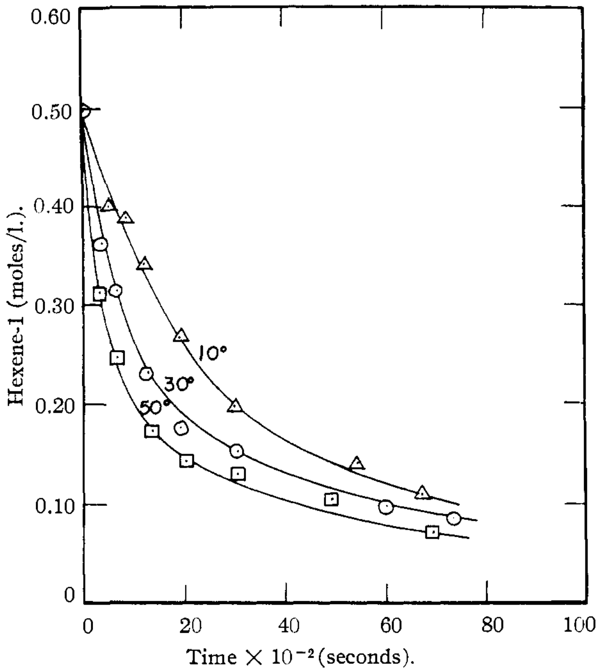

Fig. 2.—Hexene-1 polymerization, variation of rate with temperature; (catalyst, 20 mmoles $TiCl_4$, 10 mmoles Al $(i\text{-}C_4H_9)_3$; solvent, cyclohexane).

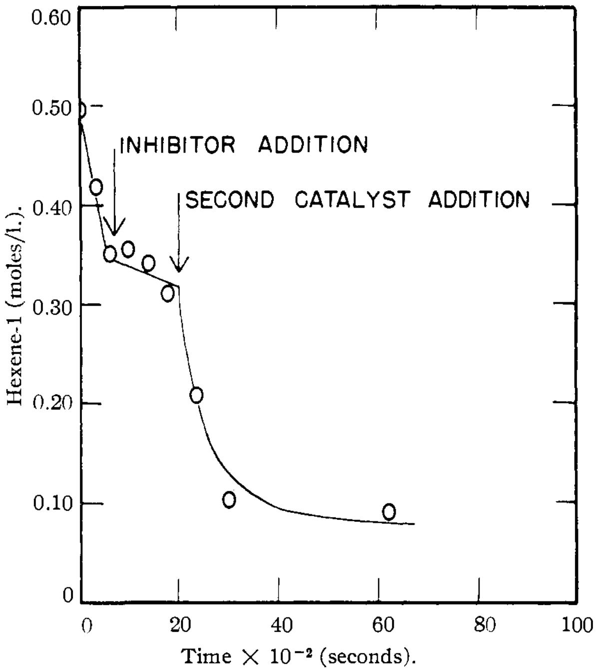

Fig. 3.—Hexene-1 polymerization at 30°. Inhibition (by triethylamine) followed by second catalyst addition (catalyst, 20 mmoles $TiCl_4$, 10 mmoles Al $(i\text{-}C_4H_9)_3$; solvent, cyclohexane).

oriented structure for catalyst ratios of 1:3 than for catalyst ratios of 2:1.

Brief mention may be made of an experiment designed to show the nature of inhibition. Early experiments showed that practically any reagent added to the reaction caused inhibition. This is particularly true of ethers, amines, ketones and alcohols. One would expect any electron donor molecule to coördinate readily with the catalyst molecules. It would be anticipated that addition of just sufficient inhibitor to complex the catalyst would lead to cessation of the reaction. Addition of fresh catalyst would be expected to start the reaction again provided the inhibitor–catalyst complex would remain as an inert substance. Results indicating that this occurs are shown in Fig. 3. Polymerization here was catalyzed at the start by 20 mmoles $TiCl_4$ and 10 mmoles $Al(i\text{-}C_4H_9)_3$. After 12.5 minutes, 2 mmoles of triethylamine was added. This amount was chosen since earlier experiments with ethylene showed that this amount would reduce the ethylene polymerization rate almost, but not quite, to zero. After 24 minutes in the dormant state, a fresh quantity of catalyst was added. This immediately recatalyzed polymerization at a rate equivalent to the initial rate.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, AMHERST COLLEGE, AND WASHINGTON AND LEE UNIVERSITY]

A New Method for the Resolution of Racemic Carbonyl Compounds: Synthesis and Use of 4-(4-Carboxyphenyl)-semicarbazide

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A new approach has been developed for the resolution of carbonyl compounds possessing an asymmetric carbon atom by means of a bifunctional intermediate which possesses a free acid group and a group which reversibly condenses with the carbonyl compound. For this purpose, 4-(4-carboxyphenyl)-semicarbazide has been synthesized and its use assayed in a successful resolution of *dl*-3-methylcyclohexanone.

Resolution *via* the carbonyl group, as briefly reviewed by Leonard and Boyer,[3] has traditionally proceeded through the preparation and use of optically active carbonyl reagents. The present investigation was undertaken to synthesize a bifunctional intermediate which would give, upon reacting with the carbonyl group, a condensate, easily hydrolyzable for regeneration of the aldehyde or ketone, and which would be able to form re-

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(2) Taken in part from theses presented by (a) George S. Denning, Jr., and O. Bertrand Ramsay to Washington and Lee University and by (b) William B. Greenough, III, to Amherst College in partial fulfillment for the degree of Bachelor of Science in Chemistry.

(3) N. J. Leonard and J. H. Boyer, *J. Org. Chem.*, **15**, 42 (1950).