Vinyl Polymerization XLVII. Polymerization of Acenaphthylene with Ziegler-Type Catalysts*

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(Received July 22, 1960)

Recently it was patented by Baxter et al.[1] that indene and acenaphthylene were polymerized in the presence of catalysts containing a titanium, vanadium or molybdenum halide in conjunction with a lithium alkyl, lithium aluminum hydride or lithium aluminum tetraalkyl. Partially crystalline homopolymers as well as copolymers of these polymers with ethylene, propylene or 1-hexadecene were described in the patent examples.

Before the patent was published, a kinetic study on polymerization of acenaphthylene in the presence of catalyst of $Ti(OBu)_4$-$AlEt_3$ or $Ti(OBu)_4$-$LiAlH_4$ was undertaken by the present authors. In this paper, the results obtained are described. In literature, polymerization of vinyl monomer with $Ti(OBu)_4$-$AlEt_3$ is found[2]. However, the system of $Ti(OBu)_4$-$LiAlH_4$ was little investigated.

Experimental

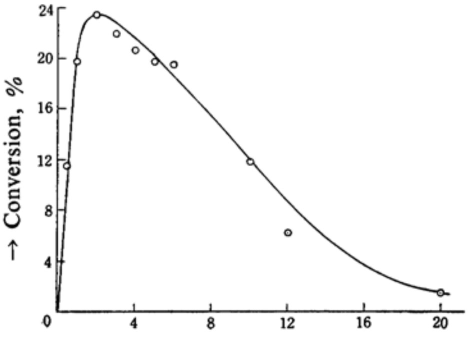
Materials.—Aluminum triethyl was obtained from Mitsui Petroleum Co. It was specified to contain 25.87% Al and 74.10% C_2H_5. The material was used without further purification. The lithium aluminum hydride was of commercial grade. *n*-Butyl titanate was prepared by the descriptions in literature[3]; b. p. 189~189.1°C (16 mmHg), Ti 13.82% (as $Ti(OC_4H_9)_4$, 14.07%). Acenaphthylene was obtained from acenaphthene by its dehyrogenation; m. p. 92~93°C, b. p., 106~107°C/3 mmHg. *n*-Heptane and toluene, pure grade, was purified as usual.

Results

Polymerization of Acenaphthylene with $AlEt_3$-$Ti(OC_4H_9)_4$.—*Procedure.*—Freshly distilled *n*-heptane was added to a 200 ml. three-necked flask with a mercury seal stirrer, an inlet tube for nitrogen and monomer, and a thermometer. The system was flushed with dry nitrogen. A solution of $(BuO)_4Ti$ in heptane and then a solution of $AlEt_3$ in heptane were added under vigorous stirring. Color appeared immediately, varying from light red to deep green. No precipitate was formed. After 10 min. stirring, the monomer solution was introduced dropwise.

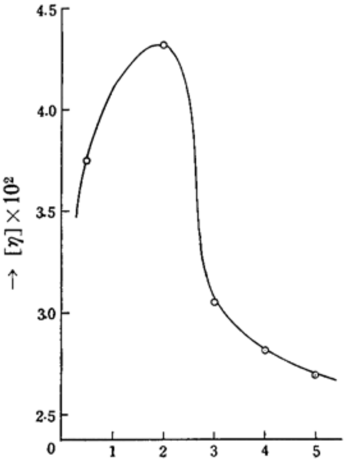
The polymerization system was poured into a large excess of methanol and the precipitate was repeatedly purified by reprecipitation from benzene solution with methanol. The polymer thus obtained contained no trace of ash.

Effects of Al/Ti Molar Ratio on Conversion of Monomer and on [η] *of Polymer.*—Keeping



→ Molar ratio Al/Ti

Fig. 1. Conversion of monomer vs. molar ratio of Al/Ti (at 80±0.5°C).



→ Molar ratio Al/Ti

Fig. 2. $[\eta]^{30°}_{\text{Benzene}}$ of polyacenaphthylene vs. molar ratio of Al/Ti.

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* XLVI of this series: M. Imoto and M. Matsuda, *High Polymer Chem.* (*Kobunshi Kagaku*), **17**, 472 (1960).

[1] W. N. Baxter, I. M. Robinson and L. H. Rombach (to duPont) U. S. Pat., 2850488, Spt. 4, 1958.

[2] N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers", Interscience Pub., New York (1959), pp. 338, 362.

[3] F. Bischoft and H. Adkins, *J. Am. Chem. Soc.*, **46**, 256 (1946).

the quantity of $AlEt_3$ constant at 0.376 g, the quantity of tetrabutyl titanate was varied. 5.00 g. of acenaphthylene was taken. The total volume was 100 ml.

Polymerization was carried out for 10 hr. The results obtained were illustrated in Figs. 1 and 2.

A maximum of conversion appeared at the molar ratio of Al/Ti of 2 : 1.

Estimation of Activation Energy. — The concentrations of aluminum triethyl and acenaphthylene were 0.376 g. and 5.00 g. in 100 ml. of the reacting solution. The molar ratio of Al/Ti was kept constant at 2 : 1. The conversions were shown in Fig. 3.

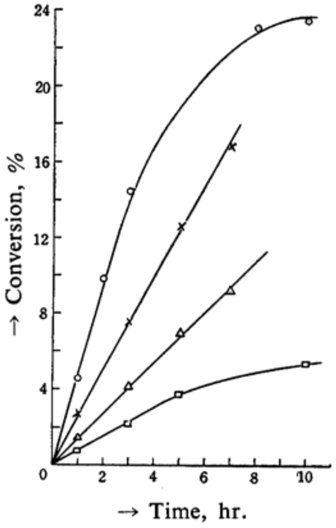

Fig. 3. Conversion of monomer vs. polymerization time.

From the slopes of the conversion curves, the initial rates of polymerisation were computed as Table I.

TABLE I. RATES OF POLYMERIZATION

	Rp(mol./l. sec.)
50±0.05°C	0.723×10^{-6}
60	1.300
70	2.438
80	4.775

From Table I the activation energy for the polymerization of acenaphthylene with $AlEt_3$-$Ti(OC_4H_9)_4$ was computed as 14.3 kcal./mol. (c. f. Fig. 4).

Using collodion film, molecular weight of a polymer was measured by the method of osmotic pressure, as shown in Table II. Intrinsic viscosity was also measured in benzene (c=g./100 ml.).

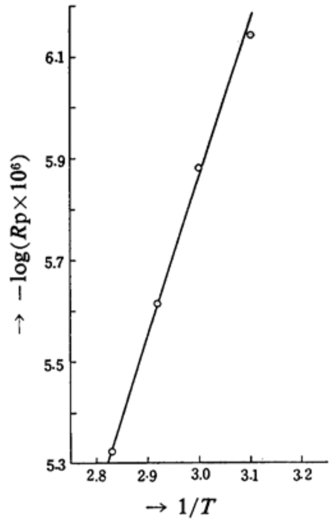

Fig. 4. Estimation of activation energy.

TABLE II.

Polymer	Mol. wt.	$[\eta]^{30°}_{\text{Benzene}}$	Literature
Al/Ti=3 : 1 80°C, 10 hr.	108000	0.035	This paper
BF_3Et_2O (60°C)	125000	0.040	Imoto, Takemoto⁴⁾

Even if polyacenaphthylene had the small value of [η], its molecular weight measured by the method of osmotic pressure was very great. As Table II shows, this characteristic figure coincided with the result obtained in the previous paper⁴⁾.

Polymerization of Acenaphthylene with $LiAlH_4$-$Ti(OC_4H_9)_4$. — In a tube, 0.0671 g. of $LiAlH_4$, 1.00 g. of acenaphthylene and various quantities of $Ti(OC_4H_9)_4$ in 10 ml. of toluene were sealed. The tubes were heated at 100±1°C for 2 hr. and then treated as described above. The results were illustrated in Fig. 5.

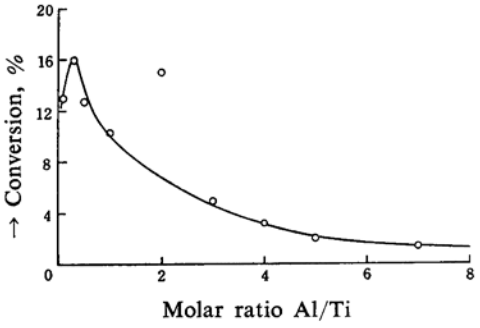

Fig. 5. Conversion of monomer vs. molar ratio of Al/Ti.

The initial rates of polymerization at several reaction temperatures were measured from the conversion curves, as shown in Fig. 6.

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4) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **15**, 271 (1955). (The value of [η] was not described.)

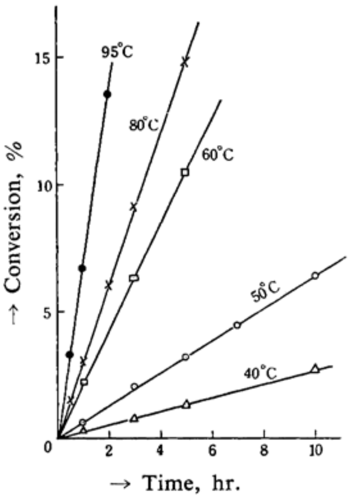

Fig. 6. Conversions of monomer at various temperatures vs. polymerization time.

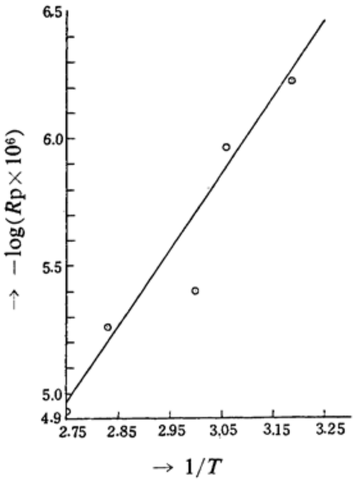

Fig. 7. Estimation of activation energy.

TABLE III. THE INITIAL RATES

Temp.	$[Rp]_0$
40±0.05°C	0.603×10^{-6} mol./l. sec.
50	1.15
60	3.99
80	5.55
95	12.2

These observations were made in the condition as follows: $LiAlH_4$ 0.25 g., acenaphthylene 1.00 g., toluene 10 ml. and the molar ratio of Al/Ti 2:1. The computed values of the initial rates are tabulated in Table III.

From the values of $[Rp]_0$ in Table III, the apparent activation energy was estimated at about 13 kcal./mol., as in Fig. 7.

After ten hours polymerization, five kinds of polymers were obtained. As to these polymers, the intrinsic viscosities were measured in benzene at 30±0.1°C and the apparent softening points were observed in sealed tubes. The results were shown in Table IV.

TABLE IV. $[\eta]$ AND SOFTENING POINTS

Temp.	$[\eta]$	Soften. pt.
40°C	0.0259	303°C
50	0.0260	305
60	0.0268	302
80	0.0278	309
95	0.0406	305

Polymerization of Styrene and Methyl Methacrylate with $LiAlH_4$-$Ti(OB_4H_9)_4$.—The procedure for polymerization was the same as that described above. 0.0256 g. of $LiAlH_4$ and 0.5 mol. equivalents of $Ti(OB_4H_9)_4$, i.e., the Al/Ti molar ratio 2:1, were used as catalyst. The temperature was 80±1°C and the duration of reaction was 20 hr. The results obtained in toluene were shown in Table V.

TABLE V.

	Methyl metacrylate g.	Styrene g.	Acenaphthylene, g.	Yield g.
Copolymerization	1.980	—	1.000	1.1235
	—	2.040	1.000	0.1065
Polymerization	1.980	—	—	0.3360
	—	2.040	—	0.6980

Summary

Polymerization of acenaphthylene was studied kinetically in heptane or toluene in the presence of titanium butanate-aluminum triethyl or titanium butanate-lithium aluminum hydride at 40~95°C. Activation energy was computed as 14.3 and about 13 kcal./mol.

Molecular weight of the polymer obtained was 125000, while $[\eta]^{30°}_{\text{Benzene}}$ was only 0.035 (c=g./100 ml.).

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