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BOOK REVIEW

Polyethylene, R. A. V. RAFF and J. B. ALLISON. Reviewed by W. E. HANFORD 126

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carbon-carbon zigzag chain has a helical structure. Considering the helical structure of this copolymer, there exist two different spacial arrangements which are possible in the ABB configuration. But the C—Cl frequencies of these two arrangements may be too close to be split.

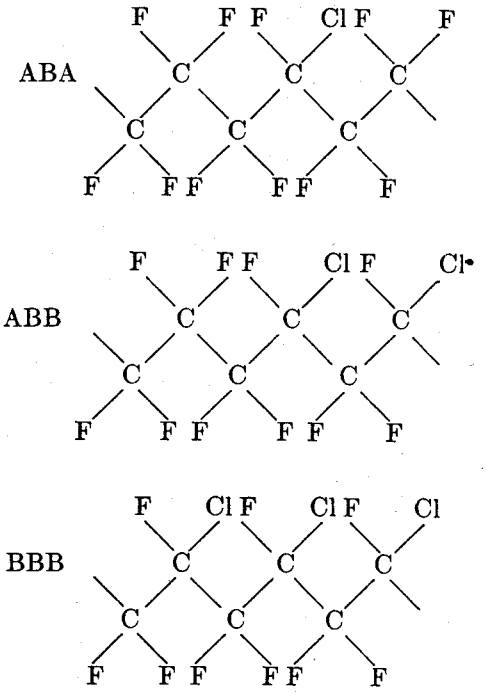

Fig. 2. Head-to-tail configurations of the TFE-TFCE copolymer.

Considering the foregoing discussion, it is clear that the changes of the infrared spectra of copolymers with the composition of the monomeric units are closely related to the arrangement of the monomeric units which has not been clarified by earlier investigations. Furthermore, the analysis of the intensities of these two bands will make it possible to determine the ratio of a portion in which TFCE monomeric units appear alone and that in which they appear in succession of two or more units. Moreover, this information can be related to the monomer reactivity ratio and also offer such interesting problems as the change of the configuration of the monomeric units with the method of polymerization or the kind of catalyzers, as well as the change of the properties of copolymers with the configuration. As this phenomenon found in the TFE-TFCE copolymers may be expected in other copolymers,[4] it is desirable to investigate the change of infrared spectra of many kinds of copolymers with the composition of the monomeric units.

The authors wish to express their sincere gratitude to Professor Masaji Kubo for his valuable advice and to Professor Yonezo Morino and Dr. Takehiko Shimanouchi for their helpful discussion on this work.

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The Nature of Some Soluble Catalysts for Low Pressure Ethylene Polymerization

Although the Ziegler process for the polymerization of ethylene[1] has been largely investigated,[2] the nature of the catalytic agents obtained by reacting a metallorganic compound with a transition metal compound is still obscure.

Recently Nenitzescu and others[3] have described some ethylene polymerization experiments carried out by catalysts prepared from $TiCl_4$ and sodium alkyls, or zinc alkyls, or aluminum alkyls. They concluded that the catalyst is a titanium organic compound, but Ziegler[4] has pointed out that the constitution of the new catalysts is much more complex than that postulated by the Rumanian authors.

Most of the Ziegler catalysts for ethylene polymerization are insoluble in the reaction medium and largely change their composition and activity by aging. Therefore they are difficult to investigate.

Recently, soluble catalysts for the low pressure ethylene polymerization have been found[5] which are less active than the best heterogeneous catalysts, but which are much more suitable for some basic researches on the chemical nature of the catalysts.

We have investigated the soluble catalytic system obtained from organoaluminum compounds and Ti compounds in which the Ti atom is bound to two cyclopentadienyl groups, and the following results have been obtained (Table I).

(*1*) By reacting $Al(C_2H_5)_3$ with $Ti(C_5H_5)_2Cl_2$ a crystalline complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$[6] has been isolated which is soluble in hydrocarbons and slowly polymerizes ethylene to high polymers at low temperature and pressure (Expt. I). The same results have been obtained by using the product of the reaction between a solution of $Al(C_2H_5)_3$ in *n*-heptane and $Ti(C_5H_5)_2Cl_2$ without separating the complex from the reaction mixture (Expt. II).

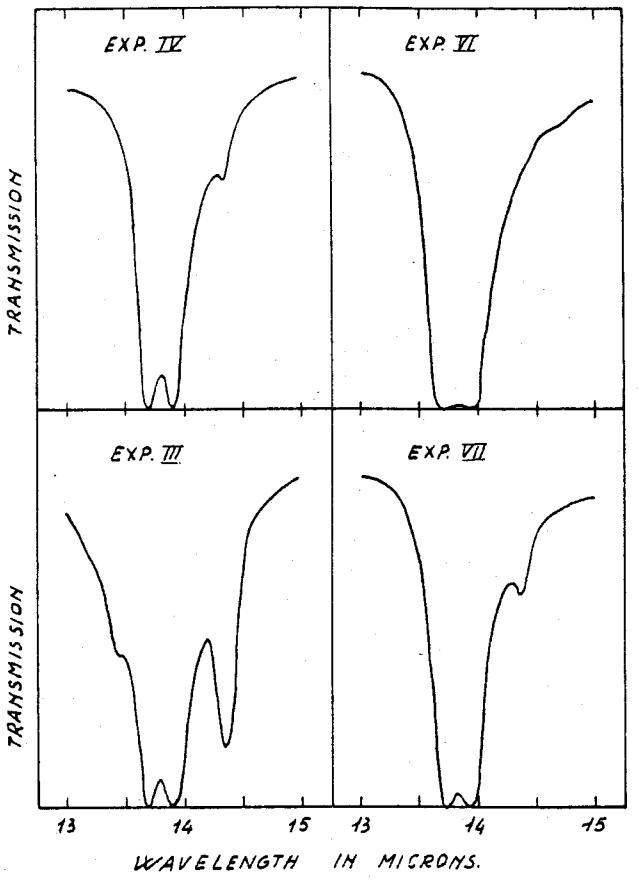

Figure 1.

(*2*) After the reaction between $Ti(C_5H_5)_2Cl_2$ and AlR_3, the cyclopentadienyl groups are still bound to the titanium atom.

(*3*) By reacting $Ti(C_5H_5)_2Cl_2$ with $Al(C_6H_5)_3.(C_2H_5)_2O$ a catalyst has been obtained which polymerizes ethylene. In the polymer $—C_6H_5$ terminal groups have been detected by IR spectra (Fig. 1) (Expt. IV). The same terminal groups have been observed by the IR method (Fig. 1) in the polyethylene produced from the heterogeneous catalyst obtained by reacting $TiCl_4$ with $Al(C_6H_5)_3.(C_2H_5)_2O$ (Expt. III).

(*4*) No polyethylene has been obtained using as catalyst $Al(C_6H_5)_3 \cdot (C_2H_5)_2O$ alone (Expt. VIII).

(*5*) No polyethylene has been obtained using as catalyst $Ti(C_5H_5)_2(C_6H_5)_2$ (Expt. V).

(*6*) By reacting $Ti(C_5H_5)_2(C_6H_5)_2$ with $Al(C_2H_5)_3$ a catalyst has been obtained which polymerizes ethylene. No phenyl groups have been detected by IR analysis (Fig. 1) in the polymer (Expt. VI).

(*7*) By reacting $Ti(C_5H_5)_2(C_6H_5)_2$ with $Al(C_6H_5)_3 \cdot (C_2H_5)_2O$ a catalyst has been obtained which polymerizes ethylene. The polymer obtained contains terminal $—C_6H_5$ groups detected by IR analysis (Fig. 1) (Expt. VII).

From these results, the following conclusions can be drawn.

TABLE I[a]

Expt.	Catalyst: Titanium compound	Catalyst: mole	Catalyst: Added organometallic compound	Catalyst: mole	Polymerization conditions: Solvent	Polymerization conditions: cm.³	Polymerization conditions: Temp., °C.	Polymerization conditions: Pressure, atm.	Reaction time, hr.	Polyethylene obtained, g	CCl_4 extractable fraction, %
I	$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	0.018	—	—	heptane	40	95	40	15	8.4	30
II	$Ti(C_5H_5)_2Cl$	0.025	$Al(C_2H_5)_3$	0.05	heptane	200	80–90	35–45	16	23	n. d.
III[b]	$TiCl_4$	0.025	$Al(C_6H_5)_3.(C_2H_5)_2O$	0.025	benzene	250	60–70	20–30	2	30	16
IV[b]	$Ti(C_5H_5)_2Cl_2$	0.025	$Al(C_6H_5)_3.(C_2H_5)_2O$	0.05	benzene	100	100–110	25–35	40	8	55
V[c]	$Ti(C_5H_5)_2(C_6H_5)_2$	0.009	—	—	benzene	130	150	50–60	24	—	—
VI[d]	$Ti(C_5H_5)_2(C_6H_5)_2$	0.006	$Al(C_2H_5)_3$	0.05	benzene	120	70–80	20–25	4	10	21
VII[b]	$Ti(C_5H_5)_2(C_6H_5)_2$	0.009	$Al(C_6H_5)_3.(C_2H_5)_2O$	0.02	benzene	120	70–80	20–21	5	15	7
VIII[c]	—	—	$Al(C_6H_5)_3.(C_2H_5)_2O$	0.067	benzene	75	150	180–200	20	—	—

[a] Phenyl groups have been recognized by the 14.36 μ band. The presence of a band at 13.45 μ accompanying the 14.36 μ band suggest that the phenyl groups are bound to $—CH_2—$ groups, and therefore are terminal groups.

[b] Phenyl groups present in the polymer.

[c] No polymer.

[d] The polymer does not contain phenyl groups.

(*1*) A crystallizable bimetallic complex has been synthesized which is a catalyst for the polymerization of ethylene.

(*2*) Catalytically active complexes of similar type can be reasonably hypothesized, although they have not been isolated, in Experiments III, IV, VI, and VII.

(*3*) Experiments III and IV show that the $(C_5H_5)_2TiCl_2$-AlR_3 catalysts polymerize ethylene at low pressure like $TiCl_4$-AlR_3, but they are less active catalysts and yield polymers having a lower molecular weight.

(*4*) In opposition to the Nenitzescu hypothesis, a Ti—C bond present in a compound containing only one metallic atom, like pure $(C_5H_5)_2Ti(C_6H_5)_2$, seems not to be able to polymerize ethylene at low pressure.

(*5*) From Experiments III, IV, VI, and VII it is seen that the organic groups initially bound to the aluminum, but not the groups bound to the titanium, appear as terminal groups in the polymer. This suggests the hypothesis that in the complex containing Ti and Al the polymerization starts at the Al—C bond.

On the basis of the above results, obtained using soluble catalysts containing the $Ti(C_5H_5)_2$ groups, we suggest that the Ziegler-type polymerization catalysts are complexes containing organometallic bonds and more than one metal atom.

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Molecular Weight and Molecular Weight Distribution of High Density Linear Polyethylene

The current interest in linear polyethylene prompted us to attempt to characterize some of these materials by application of the high temperature solution techniques developed in the course of our study of KEL-F* polymers. The material chosen for our initial efforts was a sample of high density (0.96) linear polyethylene, designated as Marlex 50.

A sample of the polymer was fractionated into seven fractions with about a 90% recovery using a high temperature fractionation technique similar to that described for KEL-F[1] with the solvent–non-solvent system being 85% 2-ethyl-1-hexanol–15% decalin as used by Wesslau.[2] The fractions were characterized by solution viscosity measurements in Tetralin at 130.0°C.

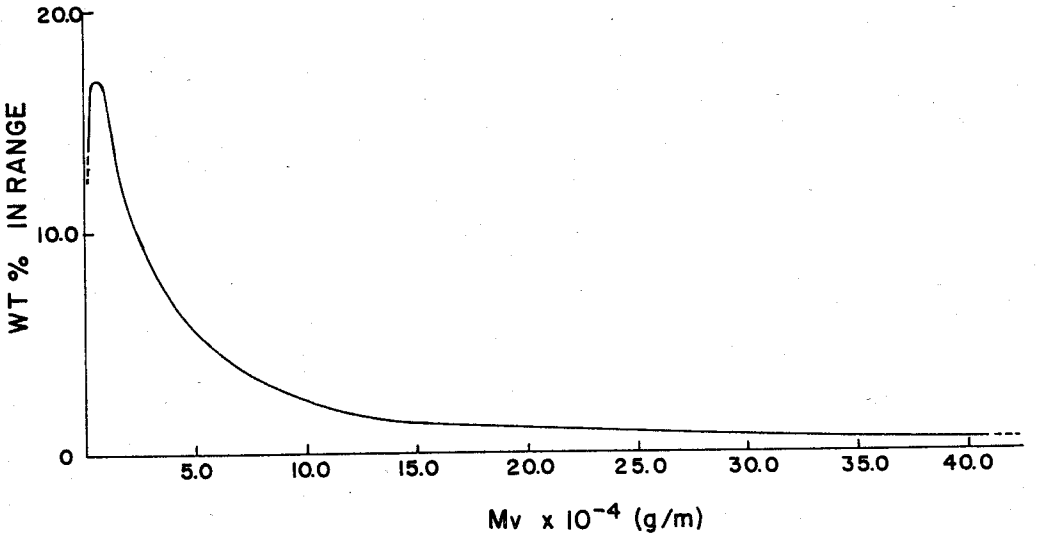

Fig. 1. Molecular weight distribution of linear polyethylene.

with corrections made for shear effects. The differential distribution curve is shown in Figure 1. In separate refractionations, the higher molecular weight ends were separated in order to provide relatively sharp fractions for osmotic molecular weight determination. The high temperature technique[3] using diethylbenzene at 110.0°C. as solvent was used for the osmotic work. The lower molecular weight fractions required some correction for diffusion while the high fractions showed no diffusion effects. The log-log plot of intrinsic viscosity *vs.* molecular weight (Fig. 2) gives the following relation:

$$[\eta] = 4.35 \times 10^{-4} \bar{M}_N^{0.76}$$

This may be compared with $[\eta] = 2.4 \times 10^{-4} \bar{M}_w^{0.78}$ given by Duch and Kuchler[4] for Ziegler-type polyolefin in Tetralin at 120.0°C. and $[\eta] =$

* KEL-F is the registered trade-mark of the Minnesota Mining and Manufacturing Company for its fluorocarbon polymers.

POLYMER NEWS

Symposium on the Physical Properties of Polymers

The Plastics and Polymer Group of the Society of Chemical Industry will hold a Symposium in London on 15, 16, and 17 April 1958 on the general subject of the Physical Properties of Polymers. The Symposium will be devoted to recent advances in:

I. The fundamental investigation of mechanical and electrical processes in polymers.
II. The physical testing of plastics, rubbers and fibres, with particular reference to dynamic and relaxation methods.

Several papers have already been provisionally accepted, and further contributions from laboratories in any part of the world are invited. Papers on the flow behavior of polymers and on the long-term stability of plastics would be particularly welcome. Offers of papers should be made to The Honorary Recorder, Mr. K. H. C. Bessant, c/o The Distillers Co. Ltd., Great Burgh, Epsom, Surrey.

Further announcement about the plans for this Symposium and the provisional programme will be published as soon as possible in *Chemistry & Industry*.

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