Copolymerization of Ethylene with Propylene of a Soluble Catalytic System (C₅H₅)₂TiCl₂—Al(C₂H₅)₂Cl in an Ethyl Chloride

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ABSTRACT: An investigation was made on the kinetics of copolymerization of ethylene with propylene in the presence of a soluble catalytic system (C₅H₅)₂TiCl₂—Al(C₂H₅)₂Cl in a medium of ethyl chloride. Two effects have been revealed: an increase in the rate of copolymerization with a rise in the concentration of propylene in the reaction zone, and the emergence of a cationic process of propylene oligomerization at the end of the copolymerization reaction. The methods of extraction, fractionation and infrared analysis were employed to obtain proof of the formation of copolymers. The conclusion regarding the single arrangement of propylene molecules in the polymeric chain was done. The reactivity ratio of monomers $r_1 = 8.7 \pm 0.5$ was determined. The physicomechanical properties of copolymers were studied and it has been shown that the addition of small amounts of propylene to the polyethylene chain (up to 1—1.5 mol %) leads to a five- to tenfold increase in the melt index, to a reduction in rigidity and the yield value by 20—30%, and to greater breaking elongations by 10—20%.

KEY WORDS   Copolymerization / Ethylene / Propylene / Dicyclopentadienyltitan Dichloride—Diethylaluminium Chloride / Ethyl Chloride / Rate / Molecular Weight / Molecular Weight Distribution / Physicomechanical Properties /

Considerable attention has been given in recent years to the problem of copolymerization of olefins in the presence of Ziegler—Natta catalysts. The overwhelming majority of research experiments were carried out using catalysts of various vanadium compounds in combination with Al-orgainc compounds. Application of a soluble catalytic system (C₅H₅)₂TiCl₂—AlR₂Cl in copolymerization of olefins was considered only in the case[1-3] of the pair of monomers ethylene—butene-1.

We pointed out earlier[4-6] that substitution of aliphatic solvents containing chlorine for aromatic solvents makes it possible to obtain from the (C₅H₅)₂TiCl₂—Al(C₂H₅)₂Cl system a polyethylene (PESC) which markedly differs from the commercial type of polyethylene in its physicochemical and physicomechanical properties.

Owing to the practically complete absence of branching and the narrow molecular weight distribution, this kind of polyethylene gives rise to certain difficulties when processed into concrete products. To modify its properties, copolymerization of ethylene with butene-1 was studied in an ethyl chloride solution; it has been established that butene-1 is an active agent in restricting the growth of polymeric chains.[3] It might be anticipated that the use of propylene as a less active agent in restraining polymeric chains would permit disclosing more distinctly the peculiarities of the copolymerization process and the influence of the α-olefin on the properties of the resultant polymers.

In this connection the investigation was carried out with the aim of studying the kinetics of copolymerization of ethylene with propylene in

a medium of ethyl chloride on the $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ system and of ascertaining the effect of small amounts of propylene incorporated in the polymeric chain on some physicomechanical properties of the polymer.

EXPERIMENTAL

The methods of the polymerization of ethylene, the purifications of ethyl chloride and ethylene, and their purity levels were described previously.[7] In these experiments use was made of propylene containing 0.3—0.4% (by volume) of propane, 5—10 ppm of oxygen and 1—5 ppm of water.

The propylene content in the initial monomer gas mixtures and in the reaction zone was analyzed chromatographically.

Measuremets of the copolymer compositions were made by the infrared spectrophotometric method. The composition was calculated by the ratio between the optical densities of the 1380 and 1460-cm^{-1} bands after the method similar to the one in ref 8; the spectra were recorded on a UR-10 spectrophotometer. The specimens for spectra recording were films ten-microns thick, obtained by the method of hot pressing at 150°C. In the case of copolymers with a low propylene content, the branching of polyethylene was measured by the intensity of the 1380-cm^{-1} band in the spectra of films 100—250-microns thick.[9] As polyethylene synthesized in the presence of the catalytic system under investigation contains practically no branchings (in general, the $CH_3/1000C$ content is less than 0.5), it may be assumed that all the methyl groups present in the copolymer belong to the propylene units.

The methods of fractioning copolymers were outlined in ref 10.

The intrinsic viscosity of polymers was measured in decalin at 135°C.

To make the physicomechanical tests, the polymer specimens were prepared by pressing at 180°C at 50 kg/cm^2, cooled at a rate of 1—2°C per minute and subjected to uniaxial extension at a rate of 100 mm/min. The dimensions of the working section of the specimen were 15 × 2.2 × (0.2—0.4) mm.

The melt index was measured on a MV-2 microviscosimeter at a temperature of 190°C

and a load of 5 kg.

RESULTS AND DISCUSSION

Kinetics of Copolymerization

At the early stage of our experiments on ethylene polymerization in the presence of propylene, as well as in the presence of butene-1, we observed the unusual nature of the kinetics of the process. As it is well known,[11] the Ziegler—Natta catalysis studied at present exhibits a drop in the total rate of copolymerization with an increase in the concentration of α-olefin in the monomer mixture (ethylene + α-olefin) and in the reaction zone. This is due to the fact the activity of an α-olefin, notably of propylene, is by two orders lower than that of ethylene.[12]

Polymerization of ethylene in the presence of propylene in an ethyl chloride medium of the $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ system does not lead to a reduced rate of the process with increasing concentration of the α-olefin in the monomer mixture; quite the contrary, the rate increases (see Figure 1). A similar pattern was observed
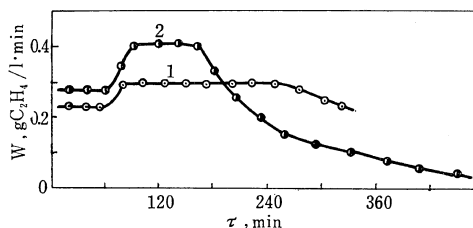

Figure 1. Kinetic curves of polymerization of ethylene and of a mixture of ethylene and 4.5% (by volume) of propylene: temp, 20°C; pressure, 300 mmHg; $[(C_5H_5)_2TiCl_2]$, 4×10^{-4} mol/l; $[Al(C_2H_5)_2Cl]$, 4×10^{-3} mol/l; (1), pure ethylene; (2), ethylene (95.5%)+propylene (4.5%).

upon polymerization of ethylene in the presence of butene-1.[3] In our case the reaction proceeds in two clearly pronounced stages: and it is evident from Figure 2 that the higher the concentration of propylene, the more noticeably displayed is the two-stage nature of copolymerization. As the propylene concentration rises, the rate increases at separate stages. For instance, whereas with a propylene concentration in the mixture
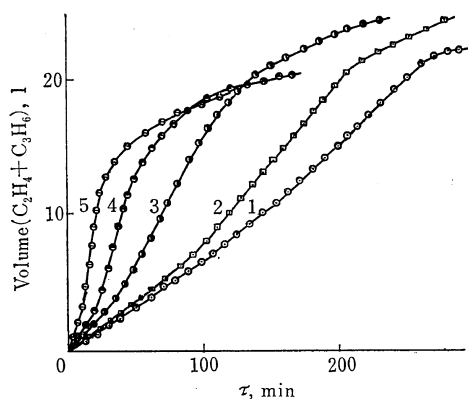
Figure 2. Kinetic curves of copolymerization of ethylene with propylene: temp, 20°C; pressure, 550 mmHg; $[(C_5H_5)_2TiCl_2]$, 4×10^{-4} mol/l; $[Al(C_2H_5)_2Cl]$, 4×10^{-3} mol. Concentration of propylene in initial gas mixture, % (by volume); (1) 1.3, (2) 2.8, (3) 7.9, (4) 14.4, (5) 17.4.

amounting to 1.3% (by volume) the ratio between the rates of the separate stages was equal to 1.4, it reached 2.3 when the propylene content was 17.4%. When the propylene concentration in the polymer chain exceeds 25%, the reaction proceeds at a high rate at the initial time period, followed by a rapid drop.

Worthwhile noting, is yet another feature of reaction of the copolymerization of ethylene with propylene. When the propylene content in the monomer mixture is above 3% (by volume), its concentration in the reaction zone rises in the course of the process and then drops practically to zero at the end of the copolymerization reaction (see Figure 3). Appreciable initial temperature rise in the reactor is recorded at the moment when the propylene content decreases in the reaction zone. It has been found that this is due to the fact that at the end of the copolymerization process there sets in a side reaction of propylene oligomerization of the products of the deactivation of the catalytic system. No polymerization of pure propylene has been observed on this catalytic system. But when small amounts of ethylene are added to the reaction zone after ethyl chloride has already been saturated with propylene, there originates a very fast process of propylene polymerization, attended with the formation of low-molecular polypropylene with a molecular weight of 400—700.

In this way ethylene accelerates such reactions occuring in the catalytic system, tending to form $AlCl_3$ which is the catalyst of the cationic polymerization of propylene. The possibility of the reaction performance with the formation of $AlCl_3$ according to the scheme
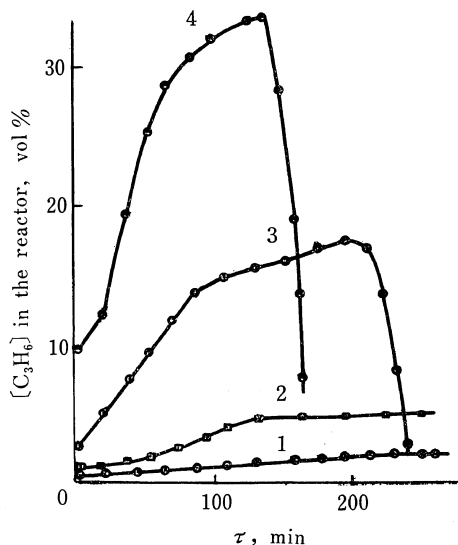

Figure 3. Change in concentration of propylene in reaction zone upon copolymerization of ethylene with propylene. See Figure 2 for experimental conditions.
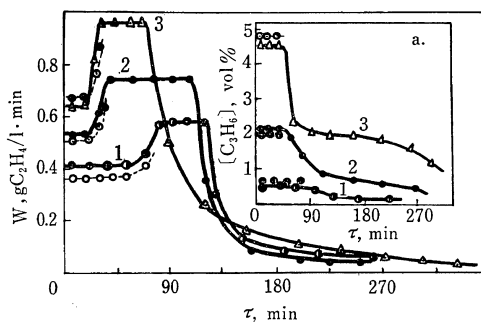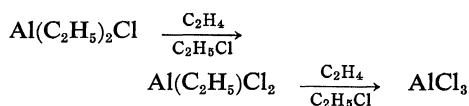

Figure 4. Kinetic curves of copolymerization of ethylene with propylene (preliminary saturation of solvent with propylene) and change in propylene concentration in reaction zone (a): $[(C_5H_5)_2TiCl_2]$, 3×10^{-4} mol/l; pressure, 360 mmHg. Propylene concentration in initial mixture, % (by volume); (1) 0.2, (2) 0.6, (3) 1.6. The dotted line (-○-○-○-) designates the experiments interrupted with the object of determining the reactivity ratio (r_2).

$$\text{Al}(C_2H_5)_2\text{Cl} \xrightarrow[C_2H_5\text{Cl}]{C_2H_4}$$
$$\text{Al}(C_2H_5)\text{Cl}_2 \xrightarrow[C_2H_5\text{Cl}]{C_2H_4} \text{AlCl}_3$$

has been shown lately.[13]

It has been established by special experiments that it is possible to select conditions for carrying out the polymerization process (saturating the solvent with propylene up to a certain concentration) when the propylene content in the reaction zone does not change during a period of up to 30 min (Figure 4). This means that the rate of supply of propylene with ethylene to the reaction zone at this period is equal to that of its joining the polymer chain. Consequently, the composition of the copolymer to be formed will also be the same as that of the incoming monomer mixture. As is known,[11] the copolymer composition is defined by the relation

$$\frac{m_1}{m_1} = \frac{(k_{11}/k_{12})/(M_1/M_2)+1}{1+(k_{22}/k_{21})/(M_1/M_2)}$$

Taking into account that $k_{22} \ll k_{11}$ and $M_2 < M_1$ (the experimental conditions are illustrated in Figure 4) there is obtained

$$\frac{m_1}{m_2} = r_1 \frac{M_1}{M_2} + 1$$

The reactivity ratio of monomers, r_1 was estimated by using the kinetic data (Figure 4) and the results of infrared analysis of the copolymer composition. It proved to equal 8.7 ± 0.5, which is approximately half the figure as compared with copolymerization of ethylene with butene-1.

Influence of Propylene on Intrinsic Viscosity and Copolymer Yield

It is well known[14] that the presence of propylene in the reaction zone during the polymerization of ethylene leads to a marked reduction in the molecular weight in view of the fact that propylene is a sufficiently active agent for chain termination.

As a matter of fact, we have established that copolymerization of ethylene with propylene results in a lower intrinsic viscosity of the resultant polymers as the propylene content rises in the monomer mixture (Figure 5). The de-
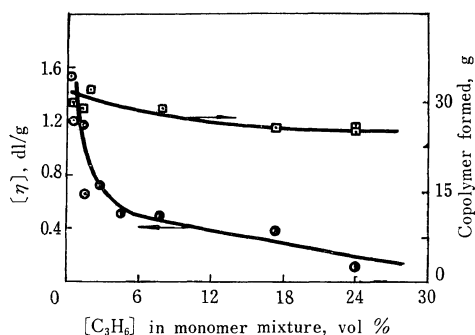

Figure 5. Influence of propylene in mixture on the molecular weight and yield of copolymers: temp, 20°C; pressure, 550 mmHg; [(C₅H₅)₂TiCl₂], 4×10^{-4} mol/l; [Al(C₂H₅)₂Cl], 4×10^{-3} mol/l. Circles (⊙, ◗) designate the values of viscosity of copolymers produced under conditions of stationary (initial) concentration of propylene in the reaction zone.

Table I. Influence of propylene concentration on the composition, intrinsic viscosity, and yield of copolymers[a]

[C₃H₆] in mixture, vol %	Yield of copolymer, g/l	Duration of experiment, min	[C₃H₆] in copolymer, mol %	[η], dl/g
1.32	94	500	0.66	1.18
2.8	109	370	2.2	0.72
7.9	97	230	5.0	0.50
14.4	83	230	7.0	—
17.4	85	159	11.5	0.40
24.3	84	107	20.0	0.12
0.2	29	75	0.2	1.20
0.2	80	270	0.3	1.52
0.54	19	40	0.56	0.99
0.54	1.2	272	0.70	1.20

[a] Temp, 20°C; pressure, 550 mmHg; [(C₅H₅)₂TiCl₂], 4×10^{-4} mol/l; [Al(C₂H₅)₂Cl], 4×10^{-3} mol/l.

pendence of the yield of the polymer on the composition of the monomer mixture, shown in the Figure 5, indicates that in spite of a considerable reduction in intrinsic viscosity, and correspondingly in the molecular weight, the yield of polymer changes less appreciably than might be expected. Therefore it may be said that the reaction of the transfer of the chain on propylene plays a substantial part in copolymerization.

From Table I (lines 7—10) where the results of the influence of proplene on the composition, intrinsic viscosity, and the copolymer yield are shown, it can be seen that on the copolymerization as well as homopolymorization of ethylene[15] an increase in intrinsic viscosity with time is observed.

Properties of PESC and of its Copolymers

Composition of Copolymers. To prove the fact that polymerization of ethylene in the presence of propylene under the given conditions leads to the formation of copolymers, and not of a mixture of two homopolymers, polymers containing different amounts of propylene were extracted by boiling n-heptane. The polymers were subjected to infrared analysis for propylene content before and after the extraction.

The resultant data are summarized in TableII.

Table II. Composition of copolymers of ethylene with propylene before and after extraction[a]

Propylene content, mol %		Amount of polymer tobe extracted, wt %
Before extraction	After extraction	
0.66	0.66	1.4
0.96	0.80	6.0
1.06	0.84	9.6
2.20	1.80	39.5

[a] Duration of extraction, 24 hr.

It is evident from Table II that with an increase in propylene concentration, the portion of the fraction soluble in n-heptane increases. In polymers subjected to extraction, the concentrations of propylene dimininish to some extent. This reduction may be accounted for by the fact that the synthesis of the copolymers

was carried out to a practically complete end of the reaction and it is therefore not precluded that the oligomerization reaction proceeded, as stated above, at the end of the copolymerization process, For this reason the propylene content in the initial polymer is slightly higher than in the one subjected to extraction. In the case that there were two homopolymers comprising a mixture then in the polymer, after extraction, no propylene would be found.

The formation of a copolymer, not of a mixture of two homopolymers, upon polymerization of ethylene in the presence of propylene is in addition attested by the results listed in Table III. It follows from the table that according to the data of the infrared analysis, the propylene content in the fractions is practically the same, that is the fractioning of the copolymers in our case took place by molecular weight only, and not by composition.

The differential curves of the molecular weight

Table III. Propylene content in fractions of copolymers of ethylene with propylene

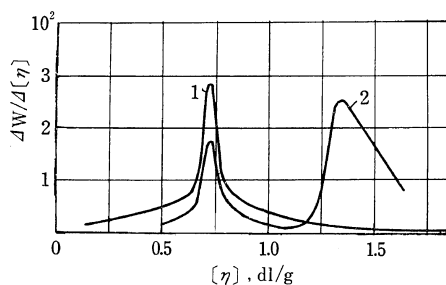| Fraction	Propylene content, mol%	
	Copolymer A	Copolymer B
1	1.0	2.9
2	0.8	3.0
3	Not determined	Not determined
4	0.75	3.2
5	0.60	Not determined
6	Not determined	3.1
7	Not determined	3.5
8	Not determined	3.5
9	1.00	Not determined
10	0.76	Not determined

Figure 6. Differential curves of molecular weight distribution of copolymers. Duration of copolymerization, min; (1) 40, (2) 270.

distribution of copolymers of ethylene with propylene are presented in Figure 6. Like polyethylene, the copolymers produced in a medium of ethyl chloride on a $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ system have a comparatively narrow-range molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.5$—3). In this case the copolymer obtained depending on copolymerization conditions may have either unimodal (curve 1) or bimodal (curve 2) molecular weight distribution.

Analysis of the infrared spectra of the products obtained through copolymerization of ethylene makes it possible to ascertain their structure. Figure 7 (3) shows a spectrum of a copolymer containing 18% of propylene. The spectrum contains an intensive 890-cm^{-1} band related to

Figure 7. Infrared spectra of polyethylene[1] and copolymers of ethylene with propylene[2,3] obtained on the system $(C_5H_5)_2TiCl_2$—$AlEt_2Cl$ in a medium of ethyl chloride. Propylene content in polymer, mol %; (1) 0, (2) 10, (3) 18.

the out-of-plane deformation mode of the CH_2 group in the vinylidene bond $CH_2=C<$, as well as a 1640-cm^{-1} band related to the stretching mode $C=C$ of this bond.

These data indicate that in the overwhelming majority of cases the termination of the polymeric chain occurs at the moment when a propylene unit is last in the chain.

$$M-CH_2-\underset{\underset{CH_3}{|}}{CH}-R \longrightarrow CH_2=C \overset{R}{\underset{CH_3}{<}}$$
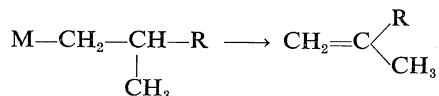
In the spectrum of pure polyethylene (Figure 7 (1)) obtained in the same conditions the copolymers, there is a 910-cm^{-1} band related to the mode of the vinyl group $CH_2=CH-$. The intensity of this band is very low since this polymer has a considerably large molecular weight. In the spectra of copolymers containing a small number of propylene units, the two bands are present, both of 910 and 890 cm^{-1}; and as propylene increases in the copolymer, the intensity of the 910 cm^{-1} band rapidly diminishes, while that of the 890 cm^{-1} band grows, the latter predominating in intensity already with a propylene content of 1—1.5%. These changes reflect the gradual alteration in the nature of the termination: with low contents of propylene the major part of the termination takes place at the moments when ethylene units are disposed at the ends of the polymeric chains, and beginning with a propylene content above 1—1.5%, the termination chiefly occurs when the propylene units are disposed at the ends of the chains.

Examination of infrared spectra also furnishes the distribution of the units in the copolymer chains with qualitative data.

As it is well known, the spectrum of crystalline polyethylene in the region of rocking modes of CH_2 groups in chains with flat zigzag conformation contains two narrow intensive bands at 720 and 730 cm^{-1}. The existence of a doublet is connected with the splitting of rocking modes in the crystalline cell of polyethylene. Examination of copolymer spectra indicates that as the propylene content increases, the intensity of the 730-cm^{-1} band abruptly diminishes and with a composition of >15% of propylene it
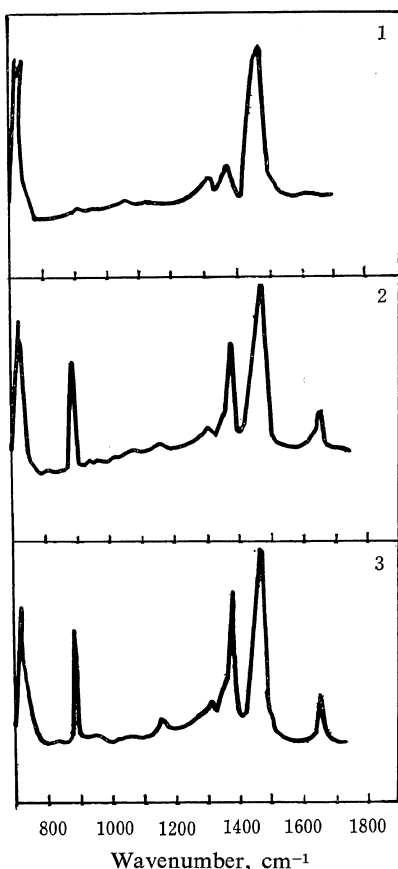
disappears from the spectra (see Figure 7). This phenomenon points to a drastic reduction in crystallinity of the polyethylene type with an increase in propylene content, which is typical of statistical copolymerization.

Figure 8 shows sections of spectra within the range of 900—1000 cm^{-1} for an ethylene—propylene copolymer produced in the presence of the catalytic system $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ in an ethyl chloride medium $[C_3H_6]$, about 18% (Figure 8 b), for an ethylene—propylene copolymer obtained* in the presence of the system $V(C_5H_7O_2)_3$—$Al(i\text{-}C_4H_9)_2Cl$ ($[C_3H_6]$ about 57%)
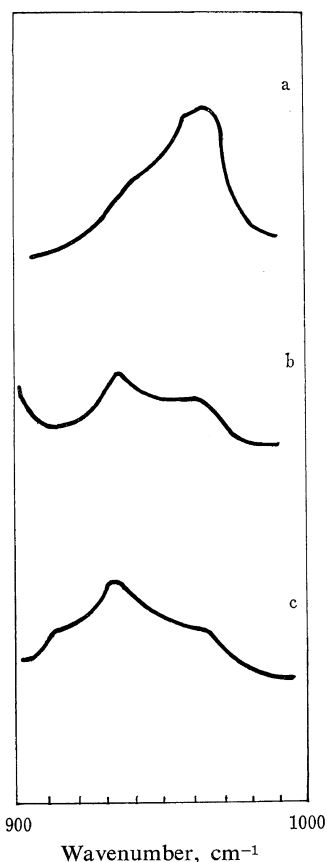

Figure 8. Infrared spectra of ethylene and propylene copolymers obtained in the presence of catalytic systems $(acac)_3V$—$Al(i\text{-}C_4H_9)_2Cl([C_3H_6]$, 57%) (a), and $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl([C_3H_6]$, 18%) (b), and of hydrogenated natural rubber (c), in the range of 1000—900 cm^{-1}.

* The copolymer was synthesized by D. M. Lisitsyn and V. V. Pebalk.

(Figure 8 a), and for hydrogenized natural rubber (Figure 8 c).** According to the data,[16] the spectrum of statistical copolymers of ethylene in the 900—1000-cm^{-1} range may be regarded as a first approximation as the superposition of the bands of propylene unit modes (primarily rocking modes of CH_3 groups) which belong to two different types of groupings: propylene blocks [rather intensive band in the 960—975-cm^{-1} band (Figure 8 a)], and of isolated propylene units surrounded by ethylene units (complex band with a maximum at 935 cm^{-1}). Such a band is to be found in the spectrum of hydrogenized natural rubber which is an adequate model of an ethylene and propylene copolymer with strict alternation of units in the chain (Figure 8 c). It can be seen from the comparison of the spectra shown in Figure 8 that in the case of an ethylene—proplene copolymer obtained in the presence of $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ the propylene links are practically completely disposed singly.

Physicomechanical Properties. The narrow molecular weight distribution and the low branching of PESC which provide it with greater rigidity and strength as compared with other
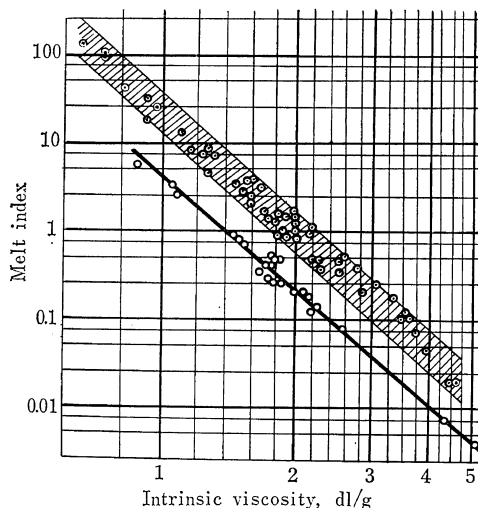

Figure 9. Dependence of the melt index of PESC and of its copolymers on intrinsic viscosity: ○, PESC; ◉, copolymers of ethylene and propopylene.

** A specimen of the polymer was kindly presented by Prof. F. Ciampelli (Italy).

kinds of polyethylene (polyethylene of low, medium, or high pressure) result in an melt index for PESC five to ten or more times smaller than for the indicated kinds of polyethylene. This creates certain difficulties in processing PESC by casting or extrusion. A higher index of PESC melt can be achieved by increasing polyethylene branching, which is effected in ethylene and propylene copolymerization.

Figure 9 shows the dependence of the melt index on the values of intrinsic viscosity for PESC and its copolymers with propylene up to 3mol %. The linearity of PESC macromolecules in the melt leads to its melt index being on the average from five to ten times lower than that of the copolymer melt. The cause of some spread of the points for copolymers appears to lie in the presence of small differences in the shape of molecular weight distribution curve.

Figure 10a shows a practically linear increase in tensile elongation of copolymers within branching of 0—10 $CH_3/1000C$. To preclude any error in interpreting the results, the copolymers were chosen with actually one and the same value of molecular weight ($[\eta] = 1.72$—1.79 dl/g). The increase in tensile elongations could be explained only by a greater part of the

Table IV. Properties of PESC and of its copolymers

Properties	PESC	Copolymer with propylene
Intrinsic viscosity, dl/g	5.0—1.5	5.0—1.5
Branching, $CH_3/1000$ C	<0.5	2—5
Density, g/cm³	0.96—0.97	0.95—0.96
Radius of spherulites, microns	10—12	8—10
Module of elasticity, kg/mm²	75—100	50—75
Yield value, kg/mm²	2.90—3.50	2.70—2.90
Elongation at beginning of flow, %	8—11	11—15
Length of neck, %	150—750	300—900
Tensile strength, kg/mm²	3.50—5.75	4.00—5.00
True tensile strength, kg/mm²	25—45	35—50
Tensile elongation, %	400—900	600—1150
Melt index at 5 kg,	0,004—0.8	0.02—4

amorphous regions. The increase in tensile strength (Figure 10b) for copolymers with branching approximately to 2 $CH_3/1000C$ from 3.8 to 4.8 (as calculated using initial cross-section of specimen) and from 36 to 45 kg/mm² (for real cross-section) may be related to both the increase in the portion of the transcrystallite chains in the intercrystallite space of the copolymer and apparently to lower deffectness of the supermolecular structure of the copolymer. At higher concentration of the propylene (over 2 mol%, which corresponds to branching over 10 $CH_3/1000C$) the true strength of copolymers does not exceed 25 kg/cm² and becomes equal to that of medium-pressure polyethylene and then of low-pressure polyethylene.

Hence, from the standpoint of physicomechanical and rheological properties, optimal for PESC, copolymerization of ethylene with propylene on the catalytic system $(C_5H_5)_2TiCl_2$—$Al(C_2H_5)_2Cl$ is to be carried out under such conditions that the propylene concentration in the copolymer should be ≤ 1mol % which correponds to branching up to 5 $CH_3/1000C$.

Table IV gives the properties of such copolymers as compared with similar properties of PESC taken, for the sake of convenient comparison, with similar characteristic viscosities.

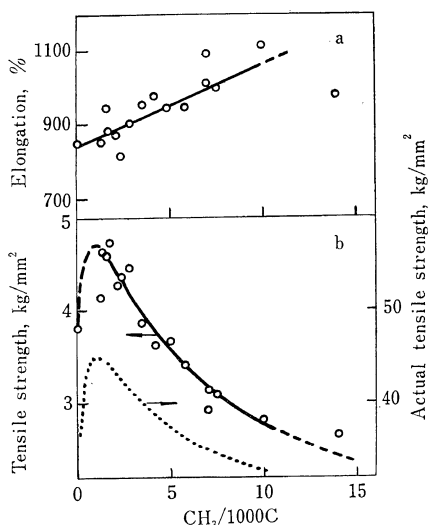It is evident from the table that branching

Figure 10. Dependence of tensile elongation (a), assumed and actual tensile strengths (b) on the branching of copolymers of ethylene with propylene: intrinsic viscosity of specimens, 1.72—1.79 dl/g.

leads to reduced density as well as rigidity of the specimens (module of elasticity, yield value, elongation at the beginning of flow). The length of the neck and tensile elongations appreciably increase, which in turn leads to the increase in true strength up to 50 kg/mm^2.

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