Preparation of soluble $TiCl_3$ catalysts by reduction of $TiCl_4$ with organoaluminium compounds and their use for copolymerization of ethylene with propylene

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Reductions of $TiCl_4$ by organoaluminium compounds were carried out in hydrocarbon and halogenated hydrocarbon solvents using various ethers as donor. Under appropriate conditions, $TiCl_4$ was quantitatively reduced by trialkylaluminium to give a homogeneous black solution of $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot$ether complex. Catalyst systems of the soluble $TiCl_3$ and $Al(i\text{-}Bu)_3$ (cocatalyst) showed high catalytic activities for random copolymerization of ethylene with propylene. The resulting copolymers were superior elastomers with low crystallinity and had outstandingly high tensile strength and elongation at break in comparison with copolymers prepared from a conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system. Characterization data of copolymers suggest that the excellent tensile properties are due to microblock-type sequences of ethylene and propylene in a polymer chain.

(Keywords: reduction; $TiCl_4$; organoaluminium compounds; soluble $TiCl_3$; random copolymer; ethylene; propylene; microblock sequences; tensile property)

INTRODUCTION

In general, solid titanium catalysts such as $TiCl_3$, $TiCl_3 \cdot \frac{1}{3}AlCl_3$ and supported $TiCl_3$ or $TiCl_4$ on $MgCl_2$ or SiO_2 show very high activity for homopolymerization of ethylene or propylene[1–5]. However, their catalytic activities for random copolymerization of the monomers are very low[6]. Moreover, the catalysts cannot copolymerize termonomers such as 5-ethylidene-2-norbornene and dicyclopentadiene. In order to enhance the activity of titanium catalysts for random copolymerization and also for copolymerization with 5-ethylidene-2-norbornene, we have studied preparations of soluble $TiCl_3$ catalysts. Recently, we have reported that soluble $TiCl_3$ catalysts, which were prepared by reduction of $TiCl_4$ with hydrogen[7,8] and by solubilization[9] of solid $TiCl_3$, enable highly random copolymerization of the monomers.

In the present study, soluble $TiCl_3$ catalysts were prepared by reduction of $TiCl_4$ with organoaluminium compounds in organic solvents, and their catalytic activities were examined for copolymerization. The copolymers obtained were characterized by i.r. and n.m.r. methods and were also tested for elastomeric mechanical properties.

EXPERIMENTAL

Materials

$TiCl_4$ (Wako Chemicals Co.), organoaluminium compounds such as $Al(Et)_3$, $Al(i\text{-}Bu)_3$, $Al(n\text{-}Hex)_3$, $Al(n\text{-}Oct)_3$, $Al(n\text{-}Dod)_3$, $Al(Et)_2Cl$, $Al(Et)_{1.5}Cl_{1.5}$ and $Al(Et)Cl_2$ (Toyo Stauffer Co.) were used without further purification. Ethers employed as donor were dibutyl ether (DBE), dihexyl ether (DHE), dioctyl ether (DOE) and didodecyl ether (DDE). Solvents used were 1,2-dichloroethane (DCE), chlorobenzene (CBz) and hexane (Wako Chemical Co.). The donors and solvents were degassed by bubbling with nitrogen and dried with molecular sieves.

Reduction of $TiCl_4$ by $Al(i\text{-}Bu)_3$

A typical procedure for the reduction is as follows. A three-necked 100 ml flask equipped with a stirring bar, a thermometer and a three-way stopcock was flushed with dry nitrogen. Under dry nitrogen atmosphere, DCE (50 ml) as solvent and $TiCl_4$ (10 mmol) were introduced into the flask by a syringe. DBE (15 mmol) as donor was added to the flask over a period of 10 min. It was allowed to stand for 30 min at room temperature, followed by addition of a solution of $Al(i\text{-}Bu)_3$ (6.8 mmol) in hexane to the flask at 3–5°C for 30 min. The contents of the flask were stirred at 3–5°C for 1 h, and then the temperature of the solution was slowly raised to room temperature. A homogeneous black solution of $TiCl_3$ was obtained.

Aliquots of the homogeneous black solution obtained were subjected to determination of the valence number of Ti. Other aliquots were used as catalyst for copolymerization of ethylene with propylene. The procedures for analysis and copolymerization were the same as in previous papers[7].

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Characterization and measurement

I.r. spectra of copolymers were recorded on a Nihon Bunko IR-A3 spectrometer. Propylene contents and crystallinities of copolymers were determined as previously[7–9]. Since the crystallinity of the copolymers was dependent on the propylene content, the comparison of crystallinities of copolymers was made by using values obtained by interpolation at a propylene content of 26.5 mol% in the plots of propylene content *versus* crystallinity.

^{13}C n.m.r. spectra were recorded at 120°C on a Nihondenshi JNM-FX-200 spectrometer. Copolymers were dissolved in a mixture of 1,2-dichlorobenzene and deuterated benzene (9 : 1, v/v) to give a concentration of 10% (w/v) for the copolymer. Tetramethylsilane was used as an internal reference. The following instrumental conditions were applied: pulse angle, 45°; acquisition time, 5 s; free induction decays, about 30000; data points, 16000. From their spectra, methylene sequence fractions of $-(CH_2)_n-$ ($n = 1, 2, 3, 4, 5$ and $\geqslant 6$) were determined by Randall's method[10]. The isotacticity of the PPP triad was evaluated from the peak intensity ratio of *mm* (21.3–22.0 ppm) to $T_{\beta\beta}$ (28.5–29.3 ppm), and triad sequences of the copolymers were determined by Cheng's method[11,12].

Gel permeation chromatography (g.p.c.) was performed at a column-oven temperature of 135°C on a Waters-150C (Waters Co.) equipped with Shodex A-807, -805, -804 and -803 columns (Showa Denko Co.), with 1,2,4-trichlorobenzene as eluent ($1.0\,ml\,min^{-1}$). The molecular weight distribution (M_w/M_n) of polymer was calculated from the g.p.c. curve using a calibration curve constructed from polystyrene standards.

Mechanical properties of copolymers were measured under the following conditions. Tensile properties: method, JIS K 6 301; instrument, Toyo-Baldwin Tensilon UTM-III-250. Hardness: method, JIS-A, JIS K 6 301; apparatus, spring-type hardness tester. Mooney viscosity: method, JIS K 6 300; instrument, Shimazu SMV-200 Mooney viscometer.

RESULTS AND DISCUSSION

Preparation of soluble $TiCl_3$ catalysts

$TiCl_4$ was reduced with various organoaluminium compounds using DCE and DOE as solvent and donor, respectively. The results are shown in *Table 1*. Trialkylaluminium compounds can reduce $TiCl_4$ to give soluble $TiCl_3$, whereas $AlEtCl_2$ and $Al(Et)_{1.5}Cl_{1.5}$ cannot reduce $TiCl_4$ satisfactorily. The extent of reduction of $TiCl_4$ seems to be associated with the acidity of organoaluminium compounds. *Figure 1* shows the dependencies of soluble Ti^{3+} yield on the molar ratio of $Al(i\text{-}Bu)_3$ and $Al(Et)_2Cl$ to $TiCl_4$. $TiCl_4$ is quantitatively reduced by $Al(i\text{-}Bu)_3$ at $[Al(i\text{-}Bu)_3]/[TiCl_4] = 0.67$ (mol/mol), while in the case of $Al(Et)_2Cl$, the optimum molar ratio is 1.0; this suggests that two alkyl groups of $Al(R)_3$ and one alkyl group of $Al(R)_2Cl$ are able to serve for the reduction. Beyond the optimum molar ratios, a green precipitate formed, and the amount of the precipitate increased with the molar ratio. Accordingly, it can be said that the selection and amount of organoaluminium compounds are very important for the preparation of soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot$ether catalysts.

The effects of solvent and donor on the reduction of $TiCl_4$ with $Al(i\text{-}Bu)_3$ were examined. As shown in *Table 2*, $TiCl_4$ is reduced by $Al(i\text{-}Bu)_3$ and solubilized in DCE or CBz (polar solvent) in the presence of a suitable donor.

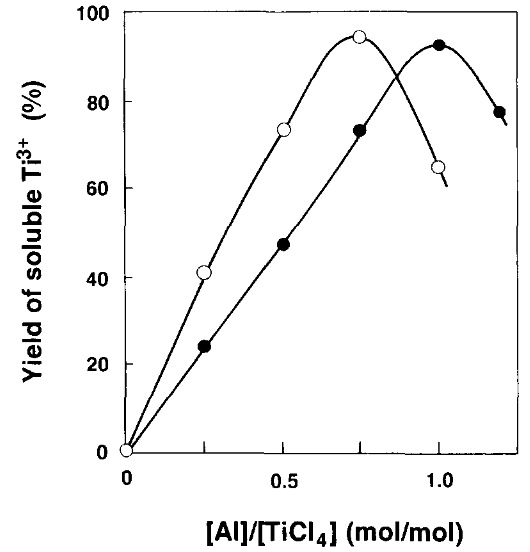

Figure 1 Plots of yield of soluble Ti^{3+} *versus* molar ratio of $[Al]/[TiCl_4]$ in the reduction of $TiCl_4$ with $Al(i\text{-}Bu)_3$ (○) and $Al(Et)_2Cl$ (●)

Table 1 Influence of organoaluminium compounds on the reduction of $TiCl_4$ and the copolymerization by resulting catalyst systems

	Catalyst preparation[a]			Copolymerization[b]		
Run no.	Al compound	Al/Ti (mol/mol)	Yield of Ti^{3+} (%)	Polymer yield (g)	Propylene units (mol %)	Crystallinity[c] (%)
1	$Al(Et)_3$	0.67	95	4.5	29	1.3
2	$Al(i\text{-}Bu)_3$	0.67	95	4.3	29	0.7
3	$Al(n\text{-}Hex)_3$	0.67	96	4.4	31	0.7
4	$Al(n\text{-}Oct)_3$	0.67	95	4.4	33	0.7
5	$Al(n\text{-}Dod)_3$	0.67	95	4.8	34	0.6
6	$Al(Et)_2Cl$	1.0	94	3.2	30	1.6
7	$Al(Et)Cl_2$	1.0	~0	0.8	9	3.9
8	None	–	–	0.5	9	4.2

[a] $TiCl_4$, 10 mmol; solvent, DCE (50 ml); donor, DOE (15 mmol); temperature, 3–5°C; time, 30 min
[b] Solvent, hexane (200 ml); soluble $TiCl_3$, 0.2 mmol (as Ti); cocatalyst, $Al(i\text{-}Bu)_3$ (2 mmol); monomer gas feed (ethylene/propylene) = $1.0/1.5\,l\,min^{-1}$; temperature, 30°C; time, 20 min
[c] Crystallinity at 26.5 mol% of propylene

Table 2 Influence of solvent and donor on the reduction of $TiCl_4$ by $Al(i\text{-}Bu)_3$ and the copolymerization by resulting catalyst systems

	Catalyst preparation[a]					Copolymerization[b]		
Run no.	Solvent	Dielectric constant ε	Donor	Donor/Ti (mol/mol)	Homogeneity of $TiCl_3$ solution[c]	Polymer yield (g)	Propylene units (mol%)	Crystallinity (%)
9	Hexane	1.88	DOE	1.5	A	2.9	19	2.1
10	Hexane		DOE	2.0	C	3.9	24	1.6
11	CBz	5.62	DBE	1.5	C	4.1	26	1.3
12	DCE	10.37	DBE	1.5	C	4.3	28	0.8
13	DCE		DBE	2.0	C	3.7	25	0.8
14	DCE		DHE	1.5	C	4.0	27	0.7
15	DCE		DOE	1.5	C	4.3	29	0.7
16	DCE		DDE	1.5	C	4.2	28	0.7

[a] Solvent, 50 ml; $TiCl_4$, 10 mmol; $Al(i\text{-}Bu)_3$, 6.7 mmol; temperature, 3–5°C; time, 30 min

[b] Same conditions as in *Table 1*

[c] A, almost soluble; C, completely soluble

Effective donors are DBE, DHE, DOE and DDE. At a molar ratio of $[donor]/[TiCl_4] = 1.5$, $TiCl_4$ could satisfactorily be reduced by $Al(i\text{-}Bu)_3$ and homogeneous black solutions of $TiCl_3\cdot\frac{1}{3}AlCl_3$·ether complexes were obtained. When hexane (non-polar solvent) was used, ethers having relatively short alkyl groups (e.g. DBE) were not effective for the solubilization of the $TiCl_3\cdot\frac{1}{3}AlCl_3$·ether complexes, because a large amount of precipitate formed. However, ethers having relatively long alkyl groups, such as DOE and DDE, were effective for the solubilization of the complexes in hexane. These brief results indicate that the solubility of $TiCl_3\cdot\frac{1}{3}AlCl_3$·ether complexes is closely correlated with the polarity of solvent and the length of alkyl group of the donor.

Copolymerization of ethylene with propylene by soluble $TiCl_3$ catalysts

The copolymerization was carried out in hexane at 30°C using soluble $TiCl_3\cdot\frac{1}{3}AlCl_3$·DOE complex catalysts prepared by reduction of $TiCl_4$ with various organoaluminium compounds. The results are listed in *Table 1*, along with data concerning the preparation of soluble $TiCl_3$ catalysts. When soluble $TiCl_3\cdot\frac{1}{3}AlCl_3$·DOE catalysts prepared by the trialkylaluminium compounds (runs 1 to 5) were used, the crystallinities of the resulting copolymers were very low, indicating high randomness of ethylene and propylene units. Also, the soluble $TiCl_3\cdot\frac{1}{3}AlCl_3$·DOE catalysts reduced with trialkylaluminium compounds having longer alkyl groups (runs 2 to 5) were more favourable for low crystallinity as compared to the catalyst reduced with $Al(Et)_3$ having short alkyl groups (run 1). On the other hand, in the case of catalysts prepared by reduction with alkylaluminium chlorides, the copolymer yields and propylene contents were very low. Furthermore, the randomness in the copolymers was unsatisfactory (runs 7 to 8).

Figure 2 shows catalytic activity as a function of the molar ratio of $Al(i\text{-}Bu)_3$ and $Al(Et)_2Cl$ to $TiCl_4$. The activity of the catalyst systems increased markedly with an increase in the molar ratio. In the case of $Al(i\text{-}Bu)_3$, the maximum point appeared at the molar ratio of $[Al(i\text{-}Bu)_3]/[TiCl_4] = 0.6$, while in the case of $Al(Et)_2Cl$, the optimum molar ratio of $[Al(Et)_2Cl]/[TiCl_4]$ was 1.0. Also, the catalytic activities in the former case were always higher than in the latter. It can be seen from a comparison of *Figures 1* and *2* that there is a good relationship between the maximum point in the catalytic activity and that in the reduction of $TiCl_4$. This fact indicates that both extent of reduction and solubility of catalyst systems are correlated with the activity of the catalyst.

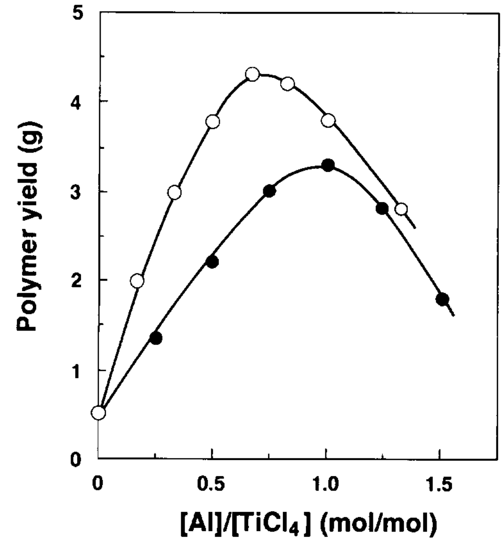

Figure 2 Plots of polymer yield *versus* molar ratio of $[Al]/[TiCl_4]$ in the copolymerization by reduced $TiCl_4$ with $Al(i\text{-}Bu)_3$ (○) and $Al(Et)_2Cl$ (●)

The plots of crystallinity of copolymer *versus* $[Al(i\text{-}Bu)_3]/[TiCl_4]$ and $[Al(Et)_2Cl]/[TiCl_4]$ (mol/mol) are shown in *Figure 3*. A minimum point exists, which represents the optimum molar ratio of organoaluminium compounds to $TiCl_4$ for the preparation of highly random copolymer. In the case of $Al(i\text{-}Bu)_3$, the minimum point appeared at a molar ratio of $[Al(i\text{-}Bu)_3]/[TiCl_4] \approx 0.5$ and in the case of $Al(Et)_2Cl$, at $[Al(Et)_2Cl]/[TiCl_4] \approx 0.75$. These values are somewhat smaller than those in the plots of soluble Ti^{3+} yield *versus* $[Al(i\text{-}Bu)_3]/[TiCl_4]$ and $[Al(Et)_2Cl]/[TiCl_4]$ (*Figure 1*). The difference may be explained by considering the following possibilities. The solubility of the catalysts should become fairly low shortly before the optimum molar ratio at which precipitate begins to form (*Figure 1*). Crystallinity would be more sensitive to solubility of the catalyst than to catalytic activity.

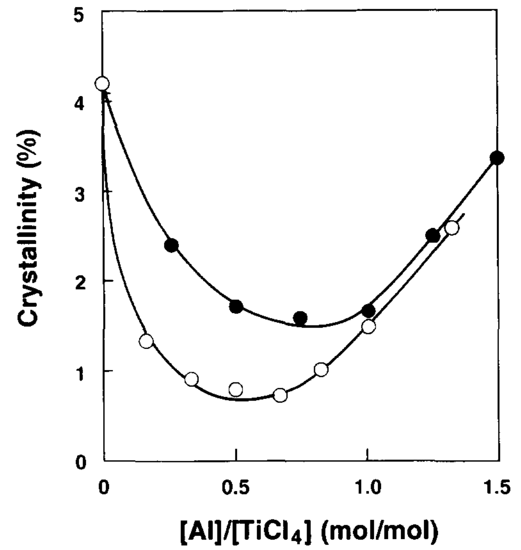

Figure 3 Relationships between crystallinity of copolymer and molar ratio of $[Al]/[TiCl_4]$ in the copolymerization by reduced $TiCl_4$ with $Al(i\text{-}Bu)_3$ (○) and $Al(Et)_2Cl$ (●)

Table 3 Microstructures of copolymers obtained using soluble $TiCl_3/Al(i\text{-}Bu)_3$ and $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst systems

Microstructure		Copolymer 1[a]	 2[b]
Propylene content (mol%)		34	46
Methylene sequence length (%)	$(CH_2)_1$	8.1	9.2
	$(CH_2)_2$	1.7	9.1
	$(CH_2)_3$	17.2	6.5
	$(CH_2)_4$	2.0	9.6
	$(CH_2)_5$	15.0	24.6
	$(CH_2)_{>6}$	56.0	41.0
Triad sequence (%)	PPP	11.4	7.0
	PPE + EPP	12.2	17.5
	EPE	14.8	18.5
	PEP	7.0	13.6
	EEP + PEE	21.9	23.2
	EEE	33.3	22.2
Isotacticity in PPP sequence[c] (%)	$P_{mm}/T_{\beta\beta}$	45.5	21.0

[a] From soluble $TiCl_3/Al(i\text{-}Bu)_3$ catalyst system
[b] From conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system
[c] P_{mm}, peak area at 21.3–22.0 ppm of *mm* sequence in propylene triad; $T_{\beta\beta}$, peak area at 28.5–29.3 ppm of propylene triad

As described in the preceding section, the combination of solvent and donor greatly affects the solubility of the $TiCl_3 \cdot \frac{1}{3}AlCl_3$·ether complexes. *Table 2* shows the effect of solvents and donors used in the reduction of $TiCl_4$ on the copolymerization. The solubility of the complexes affected not only the catalytic activity (i.e. copolymer yield) but also the propylene content and crystallinity of copolymers. That is, the higher the solubility of the catalyst, the better the random copolymerization. From the data of *Table 2*, the best combination of solvent and donor for the random copolymerization can be concluded to be DCE and DOE.

Characterization of copolymers

Measurements of ^{13}C n.m.r. were performed on copolymers **1** and **2** prepared using soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot DOE/Al(i\text{-}Bu)_3$ and conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst systems, respectively. *Table 3* shows results of the evaluation of triad sequences of the monomers and methylene sequence lengths of the copolymers from their spectra. The values of the methylene sequence fractions indicate that the degree of inversion in copolymer **1** is very low compared to that of copolymer **2**, because the methylene sequence fractions having an even number of n ($-(CH_2)_n-$: $n = 2$ and 4) result from propylene inversion. The data on isotacticity of the PPP triad in copolymer **1** show that soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot DOE$ catalysts give much higher isotactic PPP sequences than the conventional catalyst, although the propylene content of copolymer **1** is lower than that of copolymer **2**. Also, the fractions of PEP and EPE sequences (due to cross-propagation) in copolymer **1** are less than those in copolymer **2**. This suggests that copolymer **1** has many microblock sequences, the lengths of which are insufficient for the copolymer to crystallize.

Figure 4 shows the molecular weight distribution of copolymer **4** prepared by terpolymerization of ethylene/propylene/5-ethylidene-2-norbornene using a soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot DOE/Al(i\text{-}Bu)_3$ catalyst system. The value of M_w/M_n for copolymer **4** was evaluated as 4.4 from g.p.c. data. This value supports the possibility that the terpolymerization proceeds homogeneously in a similar manner to copolymerization by a $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$

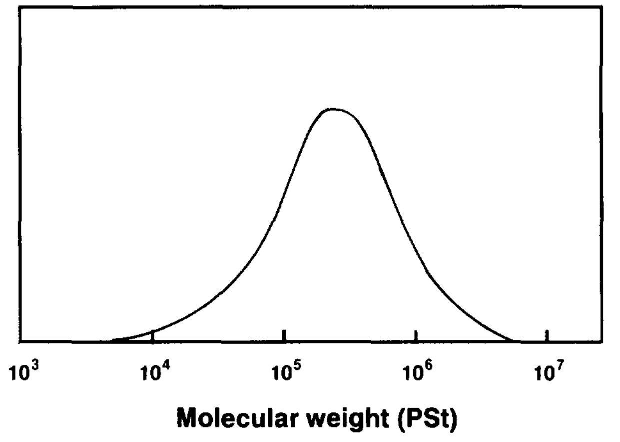

Figure 4 Molecular weight distribution of copolymer **4**

Table 4 Physical properties of uncured copolymers obtained using soluble $TiCl_4$ and $VOCl_3$ catalyst systems

Physical property	Copolymer 3[a]	 4[a]	 5[b]	 6[b]
Propylene content (mol%)	24	23	27	21
Termonomer[c] content (iodine number)	0	16	0	15
Moony viscosity ($ML_{1+4,100°C}$)	72	80	68	85
At 25°C				
Modulus at 100% (MPa)	1.3	1.4	1.1	1.2
Tensile strength (MPa)	4.8	7.2	2.1	3.9
Elongation (%)	2980	3200	1170	1990
Hardness (JIS-A)	52	56	57	55
At 50°C				
Modulus at 100% (MPa)	0.6	0.6	0.6	0.6
Tensile strength (MPa)	1.7	3.0	0.3	0.4
Elongation (%)	2870	3230	430	670

[a] From soluble $TiCl_3/Al(i\text{-}Bu)_3$ catalyst system
[b] From conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system
[c] 5-ethylidene-2-norbornene

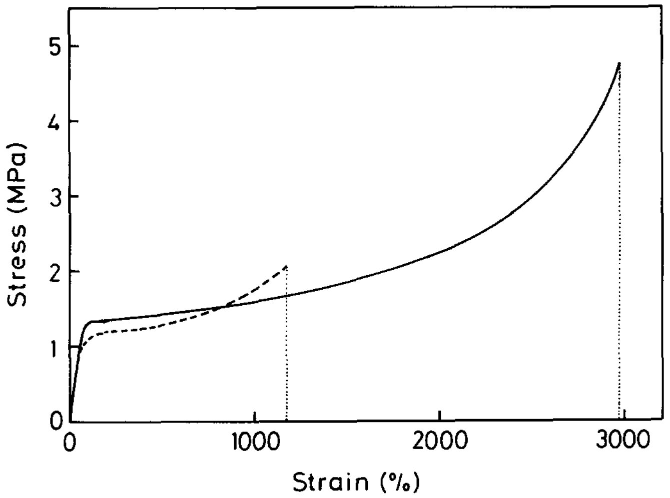

Figure 5 Stress–strain curves for copolymers **3** (——) and **5** (---) in the tensile test

catalyst system, because copolymerizations by the latter catalyst system generally give copolymers having M_w/M_n in the range of 2–10.

Some physical properties of copolymers **3** and **4** prepared using a soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot DOE/Al(i\text{-}Bu)_3$ catalyst system were measured along with copolymers **5** and **6** from a $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system. The results are shown in *Table 4*. The value of tensile strength and elongation of copolymers **3** and **4** at 25°C are 2–3 times larger than those of copolymers **5** and **6**. Moreover, at a relatively high temperature of 50°C, there was an increased difference in tensile properties between copolymers from soluble $TiCl_3$ catalyst systems and those from conventional catalyst systems; i.e. the values of tensile strength and elongation of copolymers **3** and **4** at 50°C were approximately 5–7 times greater than those of copolymers **5** and **6**. Stress–strain curves of copolymers **3** and **5** at 25°C are shown in *Figure 5*. It can be seen that the resilient energy of copolymer **3** is approximately 3 times larger than that of copolymer **5**. These excellent tensile properties of the copolymers prepared using the soluble $TiCl_3 \cdot \frac{1}{3}AlCl_3 \cdot DOE/Al(i\text{-}Bu)_3$ catalyst system may be attributed to microstructures of the copolymer, e.g. a high tacticity of the PPP triad, a low inversion content and microblock sequences.

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