Copolymerization of Ethylene and Styrene with Supported TiCl$_4$/NdCl$_3$ Catalyst

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SYNOPSIS

The copolymerization of ethylene and styrene was carried out in the presence of TiCl$_4$/NdCl$_3$/MgCl$_2$/AlEt$_3$ catalyst. The influences of comonomer ratio, concentrations of catalyst and AlEt$_3$, solvents, and temperature on the copolymerization were investigated. Copolymerization products containing styrene of 4–85 mol % were obtained with good yield. The results of ^{13}C-NMR, IR, X-ray diffraction, and solvent extraction show that the products are mainly copolymers with various comonomer sequences and exhibit special mechanical properties. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is interesting to synthesize ethylene–styrene copolymers by copolymerization of ethylene and styrene using coordination polymerization catalysts. Many authors[1-3] have reported the copolymerization of ethylene and styrene using various catalyst systems but usually with low yield or small content of styrene in the products obtained. In our laboratory, a highly active supported catalyst system composed of TiCl$_4$/NdCl$_3$/MgCl$_2$/AlEt$_3$ was developed for stereospecific homopolymerization of styrene with high yield, high catalytic efficiency, and high isotacticity.[4] In the present study, the same catalyst system was used for the copolymerization of ethylene and styrene. The influences of comonomer ratio, solvents, temperature, and concentrations of catalyst and AlEt$_3$ on the copolymerization as well as the microstructure and physico-mechanical properties of the copolymerization products were investigated.

EXPERIMENTAL

Preparation of Catalyst

Forty grams of anhydrous MgCl$_2$ was ball-milled in a 500-mL stainless jar at ambient temperature for

4 h under nitrogen atmosphere, followed by successive addition of 5 g TiCl$_4$ and 0.7 g NdCl$_3$. The mixture was continuously ball-milled for 30 h and thus the catalyst matrix was obtained. AlEt$_3$ as co-catalyst was added to activate the catalytic system prior to copolymerization.

Copolymerization

The copolymerization of ethylene and styrene was conducted in a 250-mL glass reactor equipped with a mechanical stirrer. The solvent and styrene were first introduced into the reactor. The AlEt$_3$ and catalyst matrix were added immediately; ethylene was uncontinually charged to start the copolymerization at a given temperature. When the measured amount of ethylene was exhausted, controlled within 1.5 h, and the polymerization time of 2 h was reached, the copolymerization was stopped by injecting acidified ethanol. The product obtained was washed with excess ethanol and dried at 50°C in vacuum.

Characterizations

^{13}C-NMR spectra were recorded at 100°C using a JEOL FX-90Q spectrometer operating at 22.49 MHz. Differential scanning calorimetry (DSC) measurements were made by a CDR-1 thermal analyzer at a heating rate of 10°C/min. The X-ray diffraction curves were obtained with a Regahu D/max-3A Diffraction (FeK$_\alpha$). The infrared spectra

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Table I   Effects of Monomer Feed Ratio on Catalyst Yield and Styrene Content in Ethylene–Styrene Copolymerization Products[a]

Run	1	2	3	4	5	6
Ethylene–styrene (mol)	25 : 75	33 : 67	50 : 50	67 : 33	80 : 20	90 : 10
Catalyst yield (kg/g Ti)	0.9	1.3	1.3	1.4	1.5	1.7
Styrene content in product (mol %)	85	57	40	26	13	4

[a] Polymerization conditions: [Catalyst] = 1.0 mM, [AlEt$_3$] = 5.0 mM, 50°C, 2 h, solvent: heptane.

were recorded with a NICOLET 5MX FTIR infrared spectraphotometer. The mechanical properties were tested according to the usual methods.

Fractionations were performed in a Soxhlet extractor. Butanone, chloroform, and toluene were used as solvents successively. The components of the copolymerization products were determined by elemental analysis.

RESULTS AND DISCUSSION

Copolymerization

The results given in Table I show that the copolymerization products containing styrene of 4–85 mol % were obtained with good yield and clearly indicate the speciality of the catalyst system for preparing copolymers of ethylene and styrene. NdCl$_3$ in the catalyst system seems to play a role of a promoter

for enhancing the activity of styrene. It is possible that a weak action of the f electrons of Nd in the active centers with the π electrons of styrene attracts and activates styrene molecules, consequently increases the comonomer styrene activity. Thus the copolymers containing higher styrene content were made by the present catalyst system.

The influence of catalyst concentration on the catalytic efficiency is shown in Figure 1. The catalyst yield increases with decreasing catalyst concentration. This phenomenon occurs frequently in Ziegler-type polymerizations.

Figure 2 shows the variation of catalyst yield as a function of the concentration of triethyl aluminum. It can be seen that there is an optimun triethyl aluminum concentration, i.e., 5 mM for the copolymerization to get good yield. As triethyl aluminum concentration exceeds 5 mM, the overreduction of active centers occurs, thus the yield decreases.
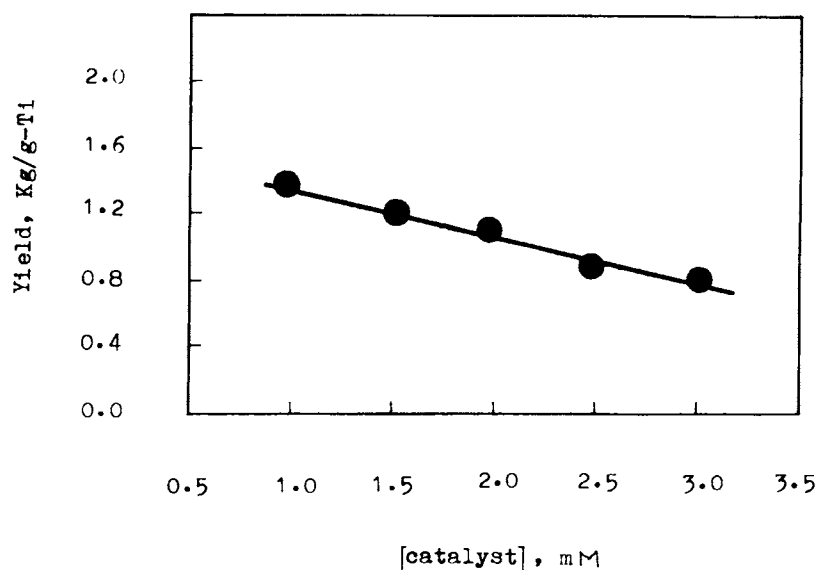
Figure 1   Influence of catalyst concentration on catalyst yield at [E]–[S] = 50:50 (mol: mol). Other polymerization conditions, see Table I.
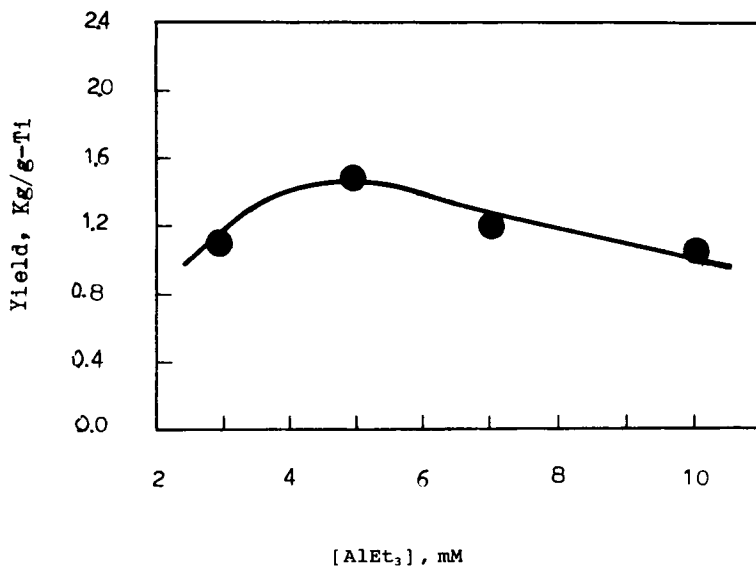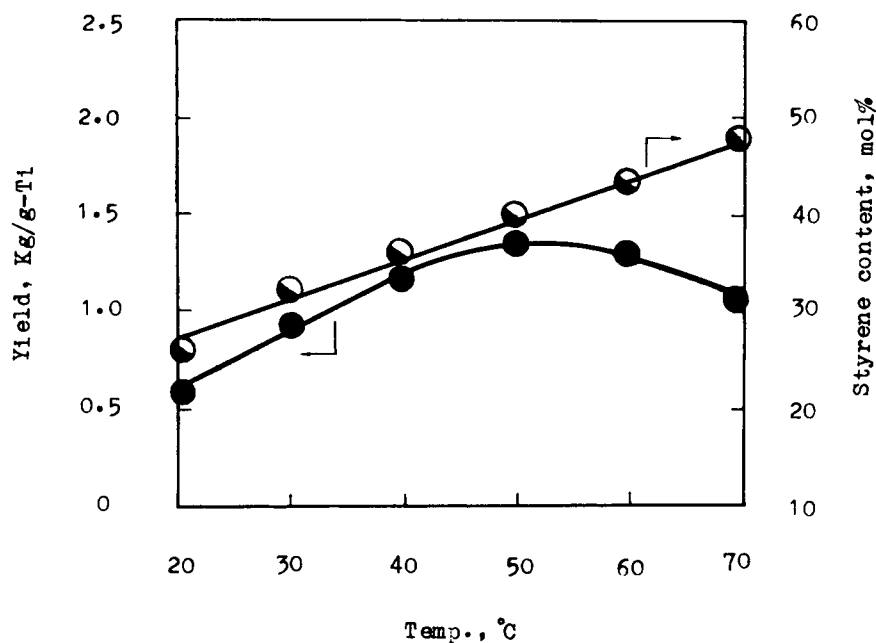
Figure 2   Influence of triethylaluminum concentration on catalyst yield at $[E]-[S]$ = 50:50 (mol:mol). Other polymerization conditions, see Table I.

The effect of temperature on the copolymerization is shown in Figure 3. The catalyst yield has a maximum value of 1.3 Kg/g Ti at 50°C and the content of styrene in the products is increased with the increase of temperature. Higher temperature is favorable to increasing the activity of styrene while lowering the solubility of ethylene in solvent.

From the results given in Table II, it is seen that

Figure 3   Influence of temperature on catalyst yield and styrene content in the copolymerization products at $[E]-[S]$ = 50:50 (mol:mol). Other polymerization conditions, see Table I.

Table II   Effects of Solvents on Ethylene–Styrene Copolymerization[a]

Run	Feed Ratio Ethylene–Styrene (mol)	Catalyst Yield (kg/g Ti)		Styrene Content in Products (mol %)	
		Heptane	Toluene	Heptane	Toluene
1	33 : 67	1.3	1.5	57	60
2	50 : 50	1.3	1.5	40	45
3	67 : 33	1.4	1.6	26	32
4	80 : 20	1.5	1.6	13	15

[a] Polymerization conditions are the same as Table I. Heptane or toluene is used as solvent.

as a solvent, toluene is better than heptane for increasing catalyst yield and styrene content in the products, since copolymerization products are more soluble in toluene than in heptane.

Fractional Extraction

The results of successive extraction for a ethylene–styrene copolymerization product (run 3 product in Table I) with boiling butanone, boiling chloroform, and hot (95°C) toluene are given in Table III. For comparison, the extractions were also done for isotactic polystyrene (iPS) and polyethylene (PE) under the same conditions.

It can be seen from Table III that after extraction with boiling butanone and boiling chloroform, iPS homopolymer has been completely removed from the copolymerization product. It is believed that the extract in the successive 95°C toluene extraction is

ethylene–styrene copolymer, as PE homopolymer is nearly insoluble in the same solvent. Thus, the copolymerization product contains at least 58.6% by weight of ethylene–styrene copolymer (E–S copolymer) since still a smaller part of copolymer possibly exists together within the insoluble residue, as indicated by the data in Table III.

IR Analysis

The IR spectra of various extracts of the copolymerization products (see Table III) are given in Figure 4. The peaks at 700 and 760 cm^{-1} arise from the out-of-plane vibrations of single substituted benzene ring. The absorption at 722 cm^{-1} is the result of the rocking vibration of $-(CH_2)_n-$ with $n > 4$. It splits into two peaks (722 and 732 cm^{-1}) for the crystalline samples. Thus the spectra in Fig-

Table III   Solvent Extractions of iPS, PE, and Ethylene–Styrene Copolymerization Product[a]
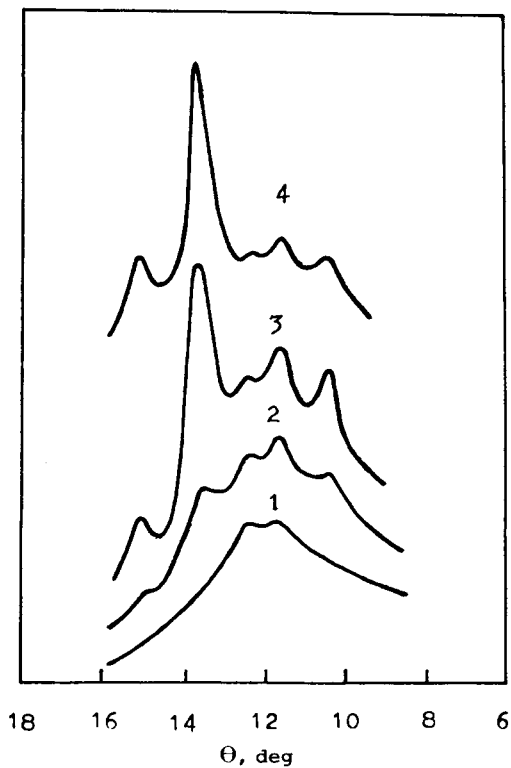
Run	Extraction Fraction	Copolymerization Product (Run 3 in Table I)	iPS	PE
1	Boiling butanone Soluble (wt %)	10.5 (100)[b]	10.2	0
2	Boiling chloroform Soluble (wt %)	19.0 (58)	89.6	1.0
3	95°C toluene Soluble (wt %)	58.6 (45)	0	1.0
4	Insoluble residue (wt %)	11.6 (10)	0	97.7

[a] All kinds of samples are prepared under the same polymerization conditions and catalyst.
[b] Styrene content (mol %) determined by element analysis for that extraction fraction.
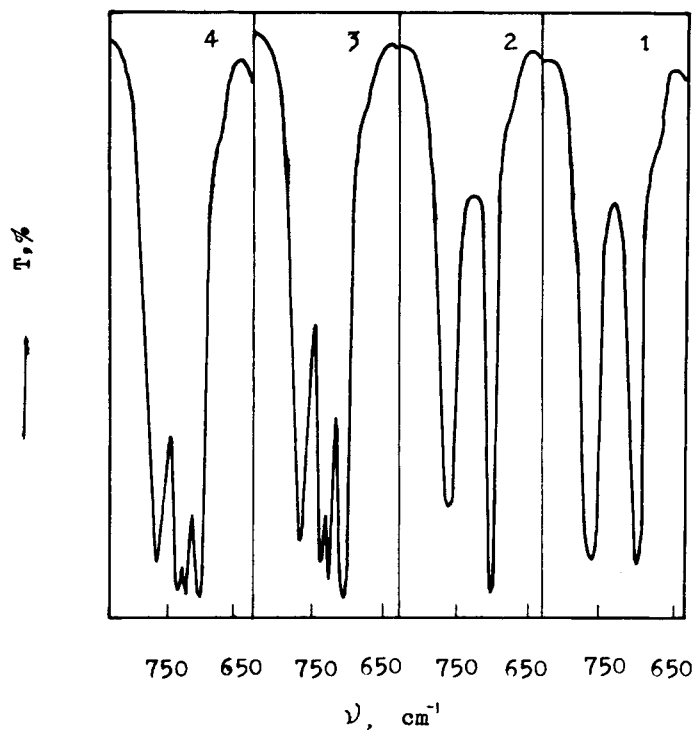
Figure 4   IR spectra of various extracts of copolymerization product run 3 in Table I. See Table III.

Figure 5   X-ray diagrams of various extracts of copolymerization product run 3 in Table I. (1) boiling butanone soluble, (2) boiling chloroform soluble, (3) 95°C toluene soluble, and (4) insoluble residue.
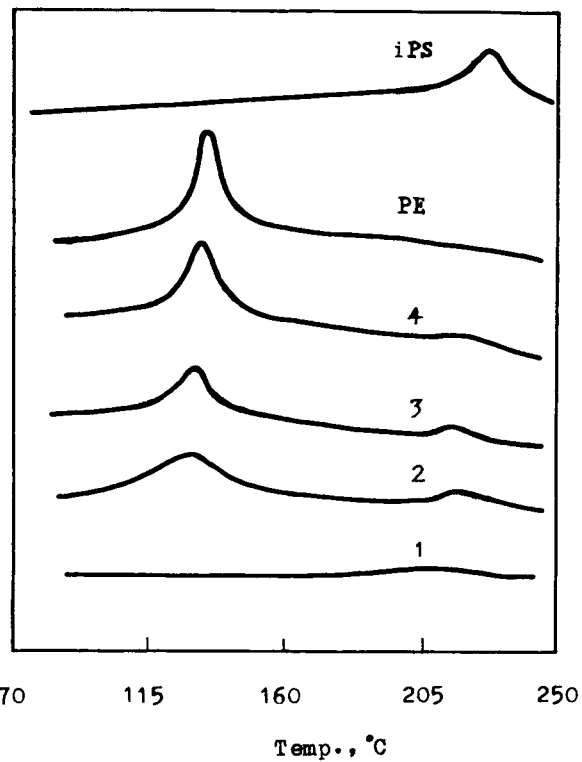
Figure 6   DSC curves of iPS, PE, and various extracts of copolymerization product run 3 in Table I. See Table III.
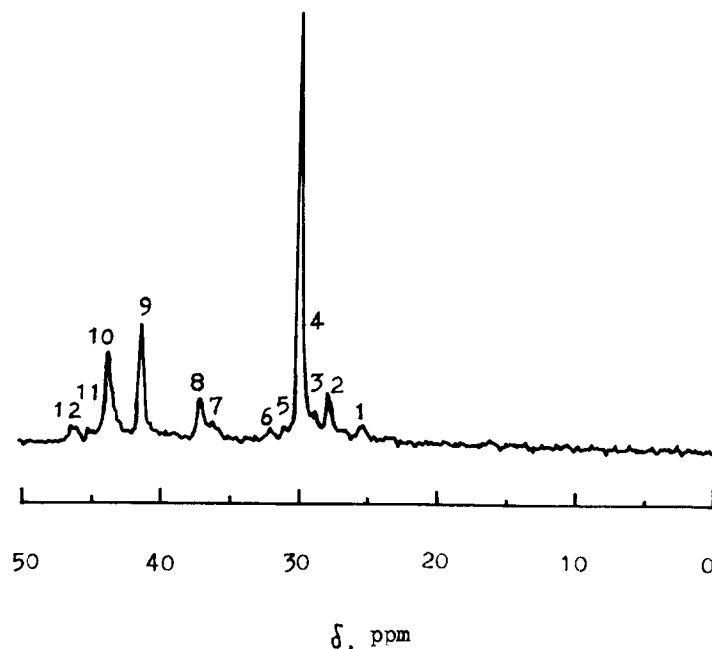
Figure 7 ^{13}C-NMR spectrum of the ethylene–styrene copolymer.

ure 4 show that the butanone extract is PS, chloroform extract is PS with small amount of ethylene units, and both of the 95°C toluene soluble and insoluble residue contain ethylene and styrene seg-

Table IV   Assignments of ^{13}C-NMR Chemical Shifts of E–S Copolymer

Sequences[a]	Carbon Type	Chemical Shifts (ppm)		
		Obsd.	Cald.[6,7]	Peak
SS	$S_{\alpha\alpha}$	43.66, 45.05	43.80	10, 11
SES	$S_{\alpha\gamma}$	36.24	36.88	7
(SEE)$_{n\geqslant1}$	$S_{\alpha\delta}$	37.18	36.88	8
SEES	$S_{\gamma\gamma}$	32.05	29.87	6
(SEEE)$_{n\geqslant1}$	$S_{\gamma\delta}$	30.80	29.87	5
(EEE)$_{n\geqslant1}$	$S_{\delta\delta}$	29.95	29.87	4
S (head) EE (head) S	$S_{\beta\gamma}$	29.10	27.88	3
(SEE)$_{n\geqslant1}$	$S_{\beta\delta}$	27.84	27.88	2
SEES	$S_{\delta\delta}$	25.30	25.89	1
ESE	$T_{\delta\delta}$	46.25	45.18	12
SSE	$T_{\beta\delta}$	43.66	43.19	10
SSS	$T_{\beta\beta}$	41.33	41.20	9

[a] S, styrene; E, ethylene.

ments that are long enough to form crystalline phases as indicated by the peak at 732 cm^{-1} and the results of X-ray diffraction and DSC shown below.

X-Ray Diffraction and DSC Analysis

Figure 5 gives the X-ray diffraction patterns of various extracts from the copolymerization product (see Table III). All of the extracts, except the butanone-soluble one, have diffraction peaks corresponding to the crystals of PE (θ = 15.10°, 13.60°, and 10.30°) and iPS (θ = 12.70° and 11.70°), respectively. The intensities of these peaks are proportional to the contents of ethylene and styrene in the extracts (see the data in brackets in Table III), indicating that the product contains long segments of ethylene and styrene. This conclusion is consistent with the results of DSC determinations as shown in Figure 6. In this figure, the tested samples (PE, iPS, and extracts of the copolymerization product) were prepared with the same catalyst and under the same conditions. It can be seen that two endothermic peaks appear in the curves of the extracts of the various copolymerization products, which may be attributed to the fusions of PE and iPS segments, respectively.

Table V   Some Mechanical Properties of HDPE, ABS, and the Copolymerization Products

| Samples	Styrene Content in Products (wt %)	Tensile Strength (MPa)	Elongation at Break (%)	Izod Impact Strength (kJ/m^2)	Hardness (N/m^2)
HDPE	—	22.1	380	4.3	50×10^6
ABS	—	22.5	160	4.4	—
Products					
1	85.6	20.1	10	0.4	136×10^6
2	67.1	21.2	67	2.3	83×10^6
3	39.2	22.0	380	10.2	58×10^6

^{13}C-NMR Analysis

The ^{13}C-NMR spectrum of the E–S copolymer (the fraction of 95°C toluene-soluble extract, see Table III) is shown in Figure 7. Assignments of the resonances are summarized in Table IV. The chemical shifts of various monomer sequences calculated according to Grant-Paul[5] and Randall[6] agree with the observed data. The resonances at 29.95 and 41.33 ppm are the reflections of ethylene-unit and styrene-unit sequences, respectively. The exact results of monomer sequence distribution are not shown here; however, the stronger intensities of these two peaks indicate that the E–S copolymer exists in a multi-block structure. Evaluated by Ray's method[7] from the intensities of dyad sequences the styrene content in this E–S copolymer is 47 mol %, approximating to the result of 45 mol % determined by element analysis (see Table III).

Mechanical Properties

Some mechanical properties of copolymerization products are summarized in Table V. By increasing the content of styrene in the products, the tensile strengths and hardness increase at the expense of impact strength and elongation. When the content of styrene is right, for example, product 3 in Table V, the impact strength is much higher that of HDPE and ABS with comparable tensile strength. The results show that the copolymerization product exhibits better mechanical properties.
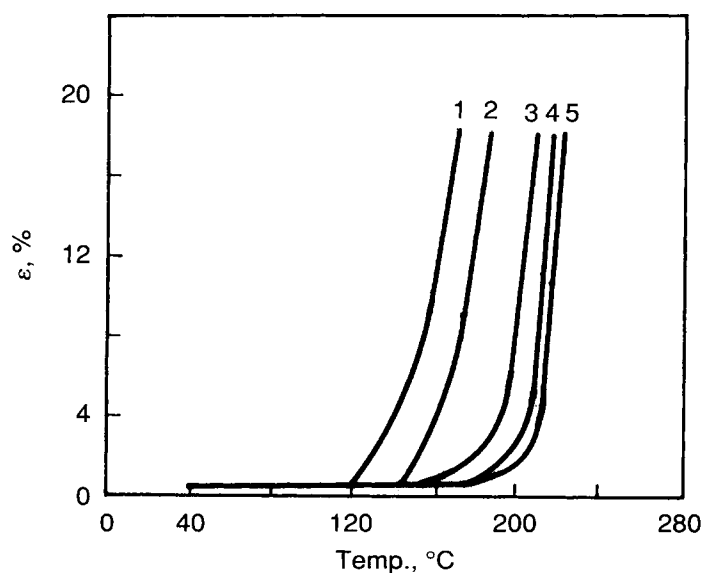
Figure 8   TMA curves of (1) HDPE, (5) iPS and copolymerization products (4) 1, (3) 2, and (2) 3 in Table V.

The thermal mechanical analysis (Fig. 8) shows that the thermal deformation temperature of the copolymerization products is located between those of HDPE and iPS and increases with styrene content. It is said that the heat resistance of PE can be rised by the copolymerization of ethylene and styrene.

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