at 220 °C for the sample having been annealed for 90 min.

As shown in Table II, the annealing of the sample in the selected condition is actually a process of further polymerization. The molecular weight of the sample increases continuously during the time, and the molecular weight distribution is approaching the theoretical value $M_w/M_n = 2$ at 100% extent of reaction.

The melting point of this polymer increases with molecular weight only when M_n is very low (Table I). It is 156 °C at $M_n = 4200$ and increases to about 200 °C when M_n is 6000. Further increase in molecular weight has little influence on the melting point of the polymer.

In contrast to the melting point, the clearing temperature of the polymer is affected to a higher extent by molecular weight (Figure 3 and Table II). An increase in the clearing temperature of 50 deg, from 225 °C for sample 1 with an M_n of 4200 to 273 °C for the sample with M_n of 13 000, was observed. It seems to us that the steady value of the clearing temperature of the polymer has not been reached after 150 min of annealing at the experimental condition.

The recurrence of birefringence of the isotropic melt of the polymer thus can be explained as a result of the increased clearing temperature, which is in turn a result of the increased molecular weight. A slower heating on the microscope means a longer annealing time. As a consequence portions of the polymer sample may have already reached a clearing point higher than the DSC value of the original sample before the latter is reached. The increasing clearing temperature during the slow observation will interfere with the observation of a clear clearing point. On the other hand, if the heating stage has been preheated to the clearing temperature before the sample is put on the stage, a complete isotropization of the melt could be observed because there would not be enough time for the polymer to grow to that of higher clearing temperature.

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Registry No. (I)(II) (copolymer), 122313-85-3; (I)(II) (SRU), 122313-86-4.

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Copolymerization of Styrene with Indene by the $Ti(O^iPr)_4$–Methylaluminoxane Catalyst

Introduction. Since the discovery of Ishihara et al.[1] that syndiotactic polymerization of styrene takes place by using some titanium compounds combined with methylaluminoxane (MAO), much attention has been paid to developing more efficient catalysts as well as to clarifying the polymerization mechanism. Similar zirconium compounds were also found to catalyze the polymerization by Zambelli et al.[2,3] More recently, Ishihara et al.[4] found that the polymerization activity is markedly improved by using $(\eta^5\text{-}C_5H_5)TiCl_3$ as a transition-metal compound. Zambelli et al.[2,5] investigated the insertion mechanism of styrene into the living zirconium–carbon bonds by ^{13}C NMR and found that 2,1-addition proceeds in this polymerization.

On the other hand, we estimated the monomer reactivity ratios of substituted styrenes from the copolymerization between styrene and substituted styrenes with the $Ti(OMen)_4$–MAO catalyst and obtained a negative value (−1.17) of ρ in the Hammett equation.[6] Besides, the copolymerization of styrene and α-olefins with the same catalyst did not give any corresponding copolymers.[6] These results might suggest that syndiotactic polymerization of styrene does not proceed via a coordinated-anionic mechanism but via a coordinated-cationic mechanism.

From such a viewpoint, we have carried out the copolymerization of styrene and indene, which is known to polymerize via a cationic mechanism,[7–12] with the catalyst system of $Ti(O^iPr)_4$–MAO.

Experimental Section. Materials. Styrene (Kanto Chemical Co., Inc.) and indene (Wako Pure Chemical Industries, Ltd.) were washed with aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. $Ti(O^iPr)_4$ (Tokyo Kasei Kogyo Co., Ltd.) was purified by distillation under reduced pressure. $AlMe_3$(TMA) and $CuSO_4\cdot 5H_2O$ were commercially obtained and used without further purification. Methylaluminoxane (MAO) was prepared from TMA and $CuSO_4\cdot 5H_2O$ according to the literature[13] and reserved as stock solution in toluene, 0.40 mmol/dm^3. Nitrogen of 99.9989% purity was used after passing through the column of 3A molecular sieve.

Polymerization and Analytical Procedures. Polymerizations were carried out in a 100-cm^3 glass reactor equipped with a magnetic stirrer. Polymereization was stopped by adding a mixture of hydrochloric acid and methanol, filtered, and dried under a reduced pressure at 60 °C. The structure and composition of the polymer were determined by ^{13}C NMR. The ^{13}C NMR spectrum of the polymer was measured at 25.1 MHz in chloroform-*d* at 60 °C with a JEOL FX-100 spectrometer. The chemical shifts were referred to HMDS added as an internal standard for $\delta = 2.0$. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Model DSC 7 at a heating rate of 10 °C/min. Gel permeation chromatograms of the polymers were obtained by Waters Model 150 GPC using standard polystyrene as reference and 1,2,4-trichlorobenzene as eluent at 140 °C.

Results and Discussion. Homopolymerizations of indene and styrene were first carried out at 60 °C with the $Ti(O^iPr)_4$–MAO catalyst, the results of which are shown in Table I together with T_g's of the polymers.

Copolymerization of styrene and indene was then conducted under similar conditions. In Figure 1 are illustrated the ^{13}C NMR spectra of syndiotactic polystyrene (a), polyindene (b), and the copolymer (c). The spectrum of (c) shows a peak attributed to the methine carbon of the styrene unit near 40.8 ppm. In addition, broadening of the peak is observed in the methine and methylene region, indicating that the polymer is not a mixture of polystyrene and polyindene but a copolymer between them. The

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Table I
Results of Polymerization of Indene and Styrene

polymer	polym time, h	polym yield, mg	styrene content, mol %	T_g, °C
polystyrene[a]	3	180		96
polyindene[b]	46	30		160
poly(styrene–indene)[c]	47	77	52.9	126

[a] Polymerization conditions: polym temp = 60 °C; styrene = 10 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 29 cm^3. [b] Polymerization conditions: polym temp = 60 °C; indene = 37 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol. [c] Polymerization conditions: polym temp = 60 °C; styrene = 3.3 cm^3; indene = 33 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol.

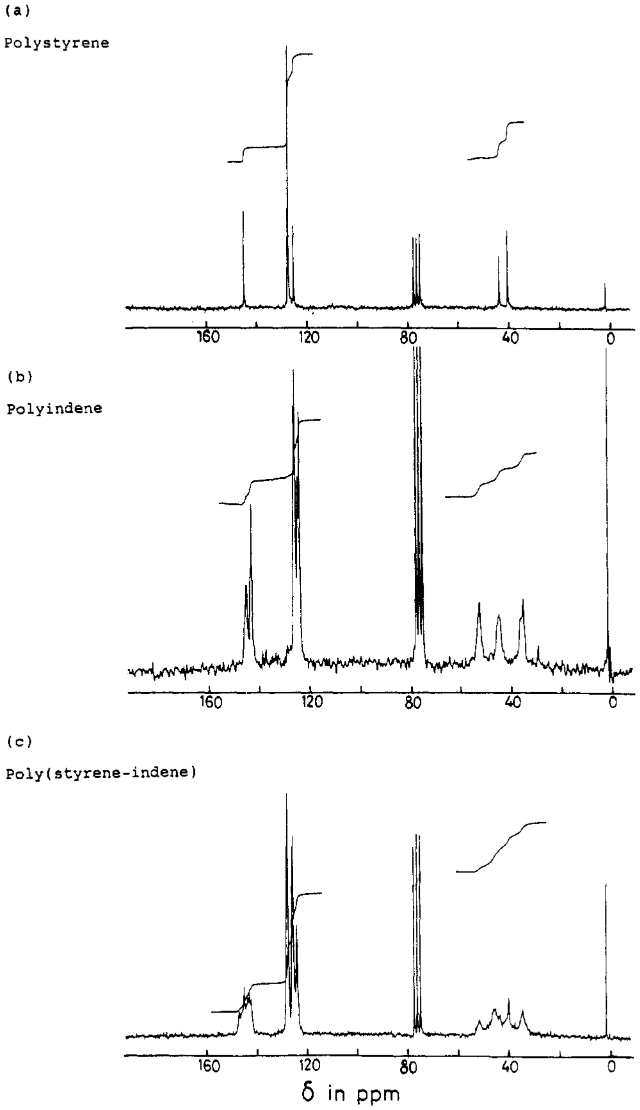

Figure 1. ^{13}C NMR spectra of the polymers. (a) Polystyrene: polym temp = 60 °C; styrene = 10 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 29 cm^3. (b) Polyindene: polym temp = 60 °C; indene = 37 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol. (c) Poly(styrene–indene): styrene content = 52.9 mol %; polym temp = 60 °C, styrene = 3.3 cm^3; indene = 33 cm^3; $Ti(O^iPr)_4$ = 0.1 mmol; MAO = 2.0 mmol.

content of styrene unit in the copolymer was calculated from the spectrum (c).

Both T_g and molecular mass distribution (MMD) were measured on the copolymer. The results obtained are shown in Table I and Figure 2. The copolymer displays a new T_g (126 °C) between those of polystyrene (96 °C) and polyindene (160 °C), and its MMD is unimodal with a very narrow polydispersity. Thus the polymer obtained from the copolymerization can be regarded as a random copolymer of styrene and indene.

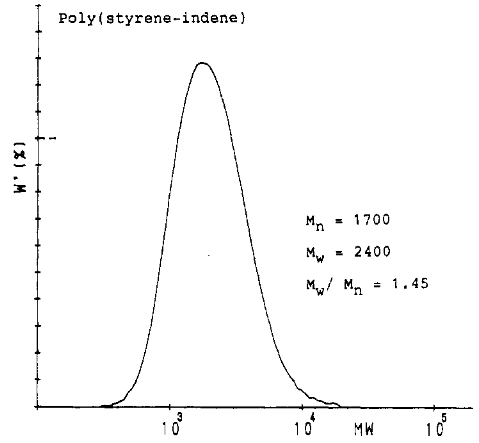

Figure 2. MMD curve of the copolymer (c).

When polymerization of styrene is carried out with usual cationic catalysts, atactic polystyrene is obtained by a cationic mechanism. Judging from both the present and previous[6] results, we propose a coordinated-cationic mechanism for syndiotactic polymerization of styrene.

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Perfect Conversion of Aspecific Sites into Isospecific Sites in Ziegler–Natta Catalysts

Introduction. The catalyst system composed of Solvay-type $TiCl_3$ and Cp_2TiMe_2 was found to show extremely high isospecificity for olefin polymerization.[1] The isospecificity of donor-free $TiCl_4/MgCl_2$ catalysts was also improved to a great extent by using Cp_2TiMe_2 as cocatalyst.[2]

Usual $MgCl_2$-supported $TiCl_4$ catalysts combined with $AlEt_3$ do not show high isospecificity, but they give at least