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Copolymerization of ethylene with styrene using the catalyst system composed of Solvay-type $TiCl_3$ and $Cp_2Ti(CH_3)_2$

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SUMMARY

Copolymerization of ethene and styrene was conducted at 40°C using the catalyst system composed of Solvay type $TiCl_3$ and $Cp_2Ti(CH_3)_2$. The crude polymer was fractionated with boiling chloroform to obtain 96.4 wt% of insoluble part, which was found to be a random copolymer of ethene and styrene. The copolymer was characterized in detail by DSC, ^{13}C NMR, etc.

INTRODUCTION

Copolymerizations of olefins and styrene using Ziegler-Natta catalysts have been reported by several authors$^{1)}$. The exact structures of copolymers, however, have not been investigated yet, which may be attributed to the complexity arising from multiple active species. Usual Ziegler-Natta catalysts contain several kinds of active species which differ in oxidation states of transition metals, stereospecificity, etc., and therefore produce not only copolymers but appreciable amounts of homopolymers.

We have recently found that the catalyst system composed of Solvay type $TiCl_3$ and $Cp_2Ti(CH_3)_2$ gives extremely high isotactic polypropylene$^{2)}$ and polystyrene$^{3)}$ (isotactic index > 99%). This catalyst system seems to have uniform active species.

From such a viewpoint, we have carried out the copolymerization of ethene and styrene by using the catalyst. Actually we obtained only copolymer as expected. This communication reports the preliminary results of the characterization of the copolymer.

RESULTS AND DISCUSSION

The copolymerization of ethene and styrene was conducted at 40°C for 15 min. to give 2.50 g of polymer. For reference, homopolymerizations of ethene and styrene were also carried out under similar conditions to obtain 1.35 g and 0.85 g of homopolymers, respectively. The crude polymer produced by copolymerization was fractionated with boiling chloroform for 6 h. The weight fractions of insoluble and soluble parts were 96.4 % and 3.6 %, respectively. The soluble part was assigned to atactic polystyrene, which might be produced by radical and / or cationic polymerization$^{4)}$.

Fig. 1a shows the ^{13}C NMR spectrum of the insoluble part. Figs. 1b and 1c display the expanded plots of regions A and B, respectively. In Fig. 1b, the resonance at 146.8 ppm can be assigned to Ph-C_1 carbon$^{5)}$. To clarify the structure of this polymer, we have supposed such a model copolymer as shown in Fig. 2 and calculated the chemical shifts by using the method reported by Wehrli and Wirthlin$^{6)}$. The calculated values are in good agreement with the observed chemical shifts. Thus, the insoluble part seems to be a random copolymer of ethene and styrene having the structure

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shown in Fig. 2, and plausible assignments are made in Figs. 1b and 1c.

The content of styrene monomer in the copolymer was estimated to be 1.0 mol% from the relative peak area ratios in the region B (Fig. 1c).

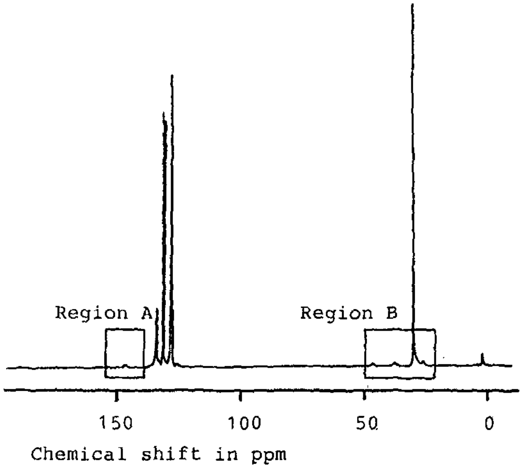

Fig. 1a. ^{13}C NMR spectrum of ethene-styrene copolymer.

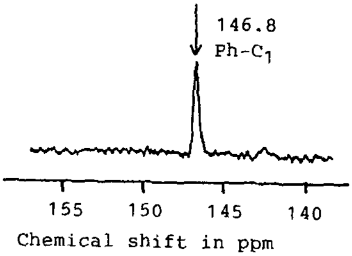

Fig. 1b. Expanded plots of region A in Fig. 1a.

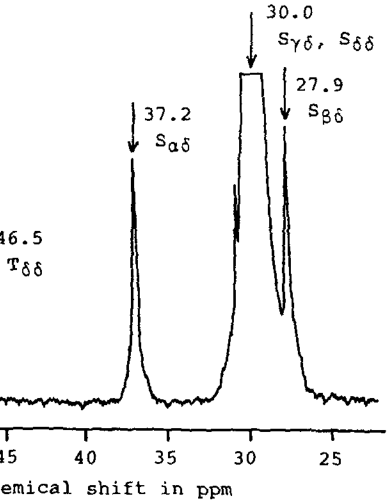

Fig. 1c. Expanded plots of region B in Fig. 1a.

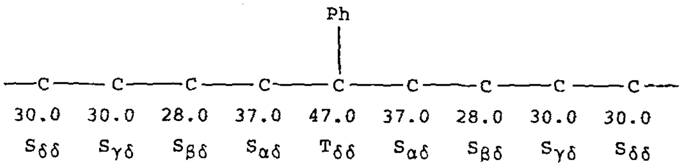

Fig. 2. Plausible structure and calculated chemical shifts of ethene-styrene copolymer.

In Fig. 3 are shown the DSC curves of both the copolymer, polyethylene and polystyrene obtained with the present catalyst system. The melting point (Tm) and the heat of fusion (ΔH_f) of the copolymer (Tm = 133°C and ΔH_f = 189J/g) are lower than those of polyethylene (Tm = 136°C, ΔH_f = 209J/g). The densities of copolymer and polyethylene were 0.948g/cm^3 and 0.960g/cm^3, respectively.

1 mol% comonomer corresponds to 5 side chains per 1000 carbon atoms in the mainchain. Thus, the effect of styrene on the density is comparable to that of 1-butene.

The MMD curves of the copolymer, polyethylene and polystyrene are shown in Fig. 4. The number-average molecular mass ($\bar{M}n$), weight-average molecular mass ($\bar{M}w$) and MMD's ($\bar{M}w/\bar{M}n$) are obtained to be $\bar{M}n$ = 179000, $\bar{M}w$ = 1582000, $\bar{M}w/\bar{M}n$ = 8.8 for the copolymer, $\bar{M}n$ = 134000, $\bar{M}w$ = 1104000, $\bar{M}w/\bar{M}n$ = 8.2 for the polyethylene and $\bar{M}n$ = 76000, $\bar{M}w$ = 650000, $\bar{M}w/\bar{M}n$ = 8.6 for the polystyrene, respectively. In spite of the considerable difference in $\bar{M}n$ and $\bar{M}w$ among the three polymers, polydispercities of these polymers ($\bar{M}w/\bar{M}n$) are not so different, which may support that three kinds of polymerizations proceed over the same active species. Broad polydispercities might be caused by the multiplicity of active species which differ only in propagating rate constants (k_p) as reported previously$^{7)}$. Starting with Mn (179000) and the styrene content (1.0 mol%), it may be calculated that one copolymer chain contains approximately 60 styrene molecules as an average.

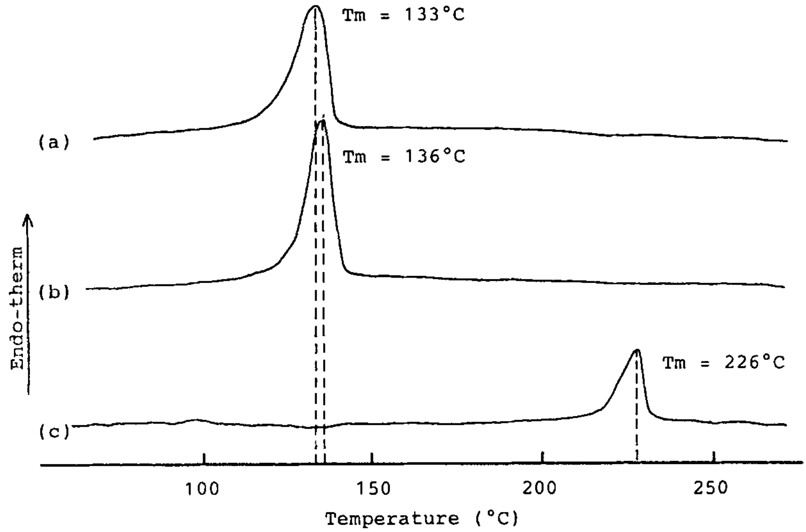

Fig. 3. DSC thermograms of the polymers obtained $TiCl_3$ and $Cp_2Ti(CH_3)_2$ catalyst system.
(a) Ethene-styrene copolymer
(b) Polyethylene
(c) Polystyrene

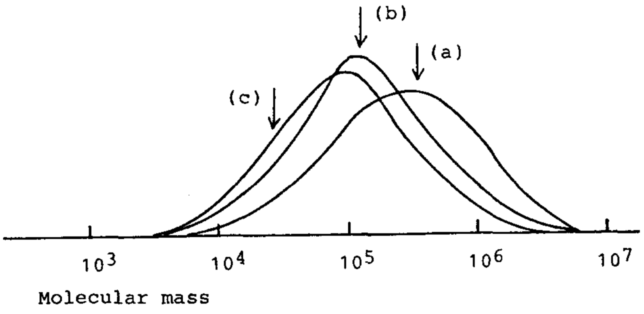

Fig. 4. MMD curves of the polymers obtained from $TiCl_3$ and $Cp_2Ti(CH_3)_2$ catalyst system.
(a) Ethene-styrene copolymer
(b) Polyethylene
(c) Polystyrene

A more detailed study is now being carried out and the results will be reported in another paper.

EXPERIMENTAL

Materials

Ethene (from Mitsubishi Petrochemical Co.) was purified by passing through NaOH and P_2O_5 columns. Solvay type $TiCl_3$ (from Showa Denko Co. Ltd.) was used without further purification. Research grade heptane and styrene were commercially obtained and purified according to the usual procedures. $Cp_2Ti(CH_3)_2$ was prepared according to the literature reported previously by Clauss et al.[8], diluted to 0.25 mol/dm^3 in heptane, and restored as stocked solutions.

Copolymerization of ethene and styrene

In a 200 cm^3 glass reactor equipped with a magnetic stirrer were placed 75 cm^3 of heptane, 25 cm^3 (240 mmol) of styrene and 2 mmol of $Cp_2Ti(CH_3)_2$. The reactor was degassed, followed by introduction of ethene. After the mixture was stirred for 10 min at 40°C, copolymerization was started by adding 1 mmol of $TiCl_3$. The polymer obtained was precipitated in excess methanol-hydrochloric acid solution, washed with methanol and dried i. vac.

Analysis of polymer

The crude polymer was fractionated with boiling chloroform for 6 h. ^{13}C NMR spectra of the polymers (10w/v% in 1,2,4-trichlorobenzene-deuteriobenzene) were recorded at 120°C using a JEOL JNH GX-500 spectrometer operating at 125.6 MHz. The chemical shift was represented in ppm downfield from internal hexamethyldisiloxane (HMDS). The molecular mass distribution (MMD) of the polymer was determined at 140°C with a Shodex LCHT-3 using o-dichlorobenzene as solvent. Differential scanning calorimetry (DSC) analysis was conducted with a Shimadzu Analyzer DT-30 and aluminum pans.

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