exclusion limits of gels had an approximately linear relationship with the difference in values of δ between the polymerization solvent and the terpolymer gels. And these results indicate that the magnitude of δ of the polymer chains of gels will control aggregation and growth of microgels in the process of gel formation.

At present we are considering whether the relationship described above can or cannot apply to both cases where the third monomer component of the terpolymer gels has about the same value of δ as AAm and has a lower value of δ than AAm. Later, we will report these results.

Conclusion. (1) The increase in molar ratio of the third monomer to acrylamide resulted in an increase in the exclusion limits of the terpolymer gels and a lowering in the values of the solubility parameters of these gels. (2) We found that the logarithm of the exclusion limits of these gels had an approximately linear relationship with the difference in the value of the solubility parameter between the polymerization solvent and the gels. (3) Obtained results indicate that the exclusion limits will be controlled by the adding of a third monomer which has a value of δ differing from that of AAm.

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Registry No. (MBAA)(AN)(AAm) (copolymer), 29825-75-0; (MBAA)(MAAm)(AAm) (copolymer), 34364-91-5.

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Ken'ichi Nakazato* and Kiichi Suzuki
School of Hygienic Science, Kitasato University
1-15-1, Kitasato, Sagamihara-Shi
Kanagawa, 228, Japan

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Preparation and Characterization of Syndiotactic Poly(vinylcyclohexane)

Poly(vinylcyclohexane) (PVCH) is expected to be useful as an engineering plastic due to its high melting point. Head-to-tail PVCH has been synthesised frequently in the past.[1] Isotactic PVCH has been prepared either by polymerization of vinylcyclohexane with Ziegler–Natta catalysts or by hydrogenation of isotactic polystyrene (PS), whereas atactic PVCH was most conveniently prepared by hydrogenation of atactic PS.[2] However, syndiotactic PVCH has never been reported so far.

More recently, Ishihara et al. have succeeded in preparing syndiotactic PS by using a kind of Kaminsky-Sinn catalyst composed of certain titanium compounds and methylaluminoxane (MAO).[3] Zambelli et al. later reported that some zirconium compounds combined with MAO are also effective for the polymerization.[4,5]

It was the objective of the present work to prepare syndiotactic PVCH by hydrogenation of syndiotactic PS.

Experimental Section. Toluene, cyclohexane, and styrene were purified according to the usual procedures. Methylaluminoxane (MAO) was prepared from $Al(CH_3)_3$ and $CuSO_4{\cdot}5H_2O$ according to the literature[6] and reserved as stock solution in toluene (0.40 mmol/dm^3).

The Ni/SiO_2 catalyst was prepared from silica gel (350 m^2/g) with an aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$; After impregnation, the catalyst was dried at ambient temperature for 8 h, dried in vacuum for 3 h at 300 °C, and then calcinated at 300 °C under 300 Torr of H_2 for 5 h. Hydrogenation of PS was carried out in cyclohexane at 200 °C for 24 h under 50 kg/cm^2 of hydrogen by using the catalyst. Polymerization of styrene was carried out in a 0.1-dm^3 glass reactor equipped with a magnetic stirrer. $Zr(OBu)_4$, 0.1 mmol, 2.0 mmol of MAO (referred to $AlMe_3$; $Al/Zr = 20$), 86.9 mmol of styrene, and 24 cm^3 of toluene were placed in the reactor under nitrogen atom room temperature. Polymerization of styrene was conducted under vigorous stirring for 3 h at 80 °C (polymer yield, 964 mg). Atactic PS was obtained from Toso Co.

The ^{13}C NMR spectra of PS and hydrogenated PS were measured in chloroform-*d* at 60 °C with a JEOL JNH FX-100 spectrometer. The chemical shifts were refered to TMS and HMDS, added as internal standards for $\delta = 0.0$ ppm and $\delta = 2.0$ ppm.

The molecular mass distribution of the polymer was measured at 120 °C with a Shodex LCHT-3 GPC equipped with a Shodex AD 80 M/S column by using standard polystyrene gels obtained from waters chromatography division. *o*-Dichlorobenzene was used as solvent. M_n and M_w were determined by standard procedures from elution curves. The glass transition and decomposition temperatures of the polymer were measured by differential scanning calorimetry (DSC) and thermogravimetry (TG)–differential thermal analysis (DTA), respectively.

DSC and TG–DTA measurements were made under nitrogen atmosphere at a heating rate of 15 K/min.

Results and Discussion. The PS obtained with the $Zr(O\text{-}Bu)_4$–MAO catalyst was confirmed by ^{13}C NMR to be highly syndiotactic. Figure 1A,B shows the ^{13}C NMR spectra of the polymers prepared by hydrogenation of syndiotactic and atactic PS. For reference, the ^{13}C NMR spectrum of isotactic PVCH reported by Zambelli et al.[7] is shown in Figure 1C. The resonances of both atactic and isotactic PVCH were assigned according to the literature.[7]

The spectrum of the hydrogenated syndiotactic PS displays no resonances in the range 120–150 ppm attributed to the aromatic C, indicating that hydrogenation of the aromatic rings was complete.

Since the hydrogenation is not expected to affect the stereochemistry of the tertiary carbon atom of the polymer chain, the hydrogenated PS should have the same stereochemistry as the original PS.

Taking the assignments of atactic and isotactic PVCH into consideration, the resonances of the syndiotactic PVCH may be assigned as indicated in Figure 1A. The weight-average molecular mass (M_w) and polydispersity (M_w/M_n) were 13 000 and 3.0 for syndiotactic PS and 102 000 and 1.02 for atactic PS, respectively. The

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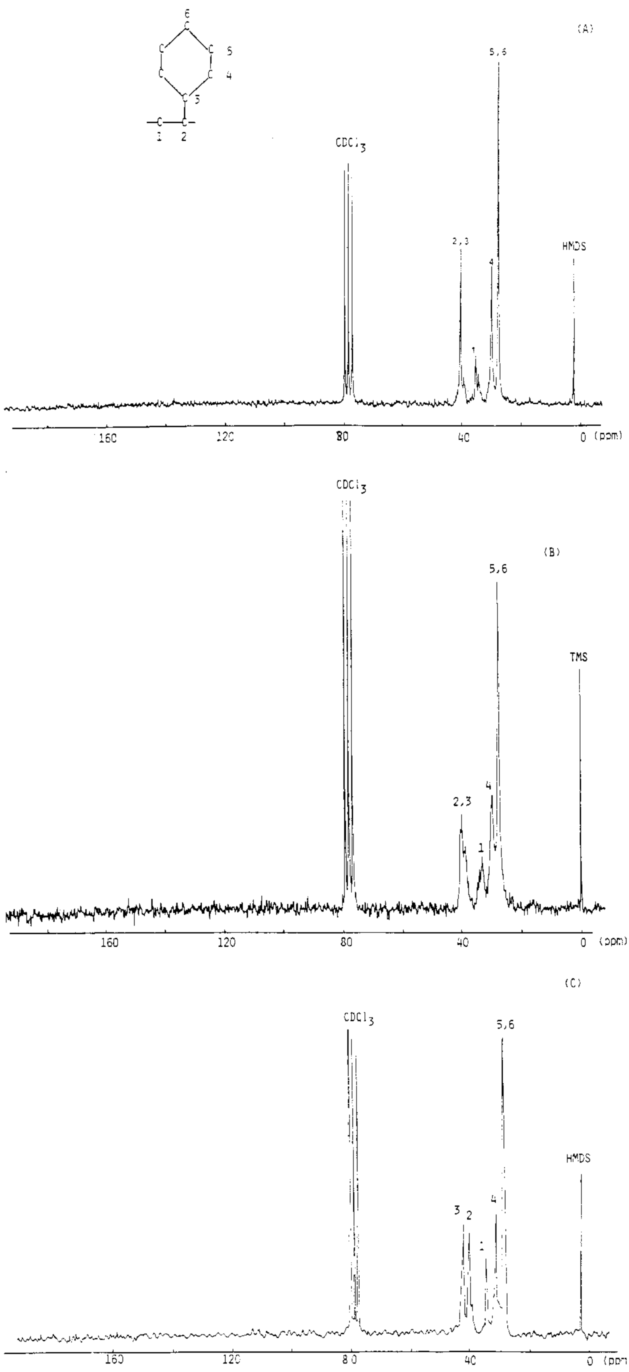

Figure 1. ^{13}C NMR spectra of PVCH. (A) syndiotactic; (B) atactic; (C) isotactic.

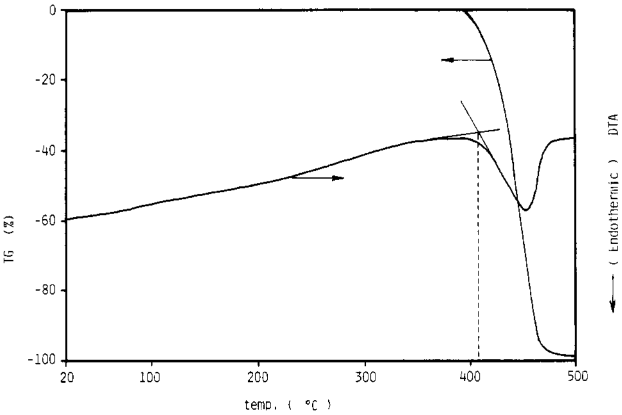

Figure 2. TG–DTA curve of syndiotactic PVCH. Sample weight, 9.03 mg.

weight-average molecular mass (MW) and polydispersity (M_w/M_n) of the syndiotactic PVCH were 6600 based on PS and 2.8. The molecular weight of the hydrogenated polymer seems to be somewhat lower, but it is uncertain at present whether degradation takes place during hydrogenation or not since we have no calibration curve for the molecular mass between PVCH and PS. Figure 2 illustrates the TG–DTA diagram for the syndiotactic PVCH, which indicates that the polymer begins to decompose near 400 °C. This decomposition temperature seems to be higher than those of atactic (368 °C) and isotactic PVCH (379 °C).[8] The glass transition temperature (T_g) of the syndiotactic PVCH determined by DSC was approximately −2.5 °C. If the polymer is crystalline, the melting temperature (T_m) can be estimated to be in the range between 132 and 270 °C from the correlation $^2/_3 < T_g/T_m < ^1/_2$. The absence of any peak in this range (Figure 2) may suggest that this polymer is not crystalline but amorphous.

Additional work is under way to characterize the syndiotactic PVCH more completely, and the results will be reported in another paper.

Registry No. $Ni(NO_3)_2$, 13138-45-9.

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Kazuo Soga,* Hisayuki Nakatani, and Takesi Shiono
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku Yokohama 227, Japan

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Temperature Ramped Fluorescence Photobleaching Recovery for the Direct Evaluation of Thermoreversible Gels

This communication concerns identification and certain fundamental quantities of reversible gels. Ferry defines a gel as "a substantially dilute solution which does not exhibit steady-state flow".[1] However, identification of gels is complicated by issues of time and spatial extent. For example, a large gel turned on its side might slowly yield to the force of gravity, appearing to flow, while a smaller gel sample of identical composition might exhibit no flow on any experimentally convenient time scale. Also, it can be difficult to distinguish a very viscous solution from a true gel in any reasonable amount of time by macroscopic methods. Even sophisticated rheological measurements do not remove the fundamental problems of mechanical perturbation and time scale from macroscopic flow measurements. There is a need for sensitive, rapid, and non-