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Stereoregular oligomers of methyl methacrylate

6. Isolation of isotactic and syndiotactic MMA oligomers from 19-mer to 29-mer by preparative supercritical fluid chromatography and their thermal analysis*

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SUMMARY

Isotactic (*it*-) and syndiotactic (*st*-) MMA oligomers from 19-mer to 29-mer could be isolated efficiently from *it*-PMMA ($\overline{DP}$ = 28.6) and *st*-PMMA ($\overline{DP}$ = 26.8) (sample load: 50 mg) by the SFC using a 10 mm *i.d.* x 250 mm column packed with silica gel. *DP* of each isolated oligomer was determined by FD mass spectroscopy, and the values agreed well with those calculated from the relative intensity of ^{1}H NMR signals due to CH_3O- and the terminal t-C_4H_9-groups. Glass transition temperature (T_g) of the *it*-28-mer measured by DSC was 34.5°C, which was higher than that of the *it*-PMMA by 6.5°C. T_g of both the *it*- and *st*-oligomers increased linearly with *DP* in the range of *DP* = 20~29. A 1 : 1 mixture of the *it*- and *st*-27-mers annealed at 140°C showed an endothermic transition at 102.3°C which was attributable to melting of stereocomplex, whereas an annealed 1 : 1 mixture of the *it*- and *st*-PMMAs had a much broader endotherm around 80 ~ 140°C.

INTRODUCTION

Synthetic polymers usually have distributions of molecular weight, stereoregularity and copolymer composition, and thus properties of a polymer sample are always observed as averaged values. It would be a great help for the fundamental studies on the structures and properties of stereoregular polymers if stereoisomers of oligomers without molecular weight distribution (MWD) are available. However, isolation of pure stereoisomers from an oligomer mixture becomes exceedingly difficult as the degree of polymerization (*DP*) increases.

Recently, we found the highly isotactic (*it*-) and highly syndiotactic (*st*-) living polymerizations of MMA initiated with t-C_4H_9MgBr [1] and t-C_4H_9Li-trialkylaluminum complex [2], respectively. The living polymerization systems provide the stereoregular oligomers with a narrow MWD and with a well-defined chemical structure. The purely *it*- and purely *st*-oligomers from the dimer to octamer could be isolated with the aid of the HPLC technique, using silica gel as a stationary phase and butyl chloride / acetonitrile as a mobile phase [3], from the oligomer mixtures [4,5]. The pure oligomers were

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analyzed by NMR spectroscopy [4] and by X-ray single crystal determination [5]. Isolation of the oligomers exceeding the decamer level needs a more effective means of separation such as supercritical fluid chromatography (SFC). Application of SFC to the separation of oligomers has been widely studied [6,7], although few papers [8~10] reported its preparative use. In this work, the *it*- and *st*-oligomers from 19-mer to 29-mer were isolated by SFC, individually, and their thermal properties were investigated.

EXPERIMENTAL

Preparation of the MMA oligomers

The low molecular weight *it*-PMMA : Living isotactic polymerization of MMA was initiated with t-C_4H_9MgBr ([MMA]/[t-C_4H_9MgBr] = 20 mol/mol) in toluene at -78°C [1], and the reaction was terminated 24 h after the initiation by adding a small amount of phenol dissolved in toluene to the polymerization mixture [11]. The termination by phenol is necessary for the formation of isotactic dyad at the chain-end of the oligomers. The mixture was poured into hexane and the insoluble part (87.3 % yield, $\overline{DP} = 28.6$, $\overline{Mw}/\overline{Mn} = 1.15$, $mm : mr : rr = 96.1 : 3.9 : 0$) was subjected to fractionation by SFC.

The low molecular weight *st*-PMMA : Living syndiotactic polymerization of MMA was carried out with t-C_4H_9Li/(n-C_4H_9)$_3$Al complex ([Al]/[Li] = 3/1 mol/mol, [MMA]/[t-C_4H_9Li] = 20 mol/mol) in toluene at -93°C [2], and the polymerization reaction was terminated with toluene solution of *t*-butanol 24 h after the initiation. The termination by *t*-butanol gives high syndiotacticity at the chain-end dyad [11]. The polymerization mixture was poured into hexane and the insoluble part (80.7 % yield, $\overline{DP} = 26.8$, $\overline{Mw}/\overline{Mn} = 1.09$, $mm : mr : rr = 0.3 : 7.6 : 92.1$) was subjected to the SFC fractionation.

Conditions of SFC

SFC was performed on a JASCO SUPER-200 chromatograph equipped with a Hewlett-Packard 5890 column oven. A 10 mm *i.d.* x 250 mm column packed with silica gel (Develosil 100-5, Nomura Chemical Co., Ltd., particle size 5 μm) was used. The system consists of two pumps, one is for the delivery of liquefied CO_2 as a mobile phase (flow rate = 7.5 ml/min), and the other for the delivery of ethanol as a modifier (flow rate = 2.1 ml/min). Concentration of the modifier in the mobile phase was kept constant throughout the experiments. The fluid pressure was controlled by a back-pressure regulator to 202 ±1 kgf/cm^2. The initial column temperature was adjusted to 100°C and the column temperature was lowered at a rate of 2°C/min to 40°C. Chromatogram was recorded using a UV detector operated at the wave length of 220 nm.

Measurements

Mass spectra were recorded on a JEOL JMS-DX303HF operated at the field-desorption (FD) mode.

^1H and ^{13}C NMR spectra were measured in nitrobenzene-d_5 at 110°C and in chloroform-d at 55°C, respectively, on a JEOL JNM-GX500 spectrometer (^{1}H: 90° observation pulse, pulse repetition = 20 s, 128 scans; ^{13}C: 45° observation pulse, pulse repetition = 3.0 s, 14000 or 15000 scans).

Differential scanning calorimetry (DSC) was performed on a Rigaku DSC-8230 apparatus. Glass transition temperature (T_g) and melting temperature (T_m) were determined from the thermograms recorded at a heating rate of 10°C/min using samples of 2 mg each packed in an aluminum container. Immediately before each measurement, the sample was heated to 150°C and then cooled rapidly to -80°C.

RESULTS AND DISCUSSION

Isolation of the pure it- and st-oligomers of MMA

Figure 1a shows an SFC curve of the *it*-PMMA ($\overline{DP}$ = 28.6, $\overline{Mw}/\overline{Mn}$ = 1.15) prepared with *t*-C_4H_9MgBr. The oligomer components from 10-mer to 59-mer separated completely. The amount of the sample injected on the silica gel column was 50 mg (100 μl of 50 w/v% acetone solution). In our previous paper [10], SFC separation of the MMA oligomer with $\overline{DP}$ of 9.9 was performed using octadecylsilane-treated (ODS) silica gel as a stationary phase (reverse phase conditions) and the maximum sample-load was 0.3 mg for a 1.7 mm *i.d.* x 250 mm column. Much less amount of the sample could be injected on the ODS silica column when $\overline{DP}$ of the oligomer exceeded 20. The present result has indicated that the bare, unbonded silica (normal phase conditions) is more effective than ODS silica for the separation of MMA oligomers.

The fractions from 19-mer to 28-mer (Figure 1a) were collected for several times. The delay of the timing for the fractionation was estimated as approximately 1.0 s from the flow rate and the volume of the connecting path between the detector and the back pressure regulator (160 μl). The fraction of

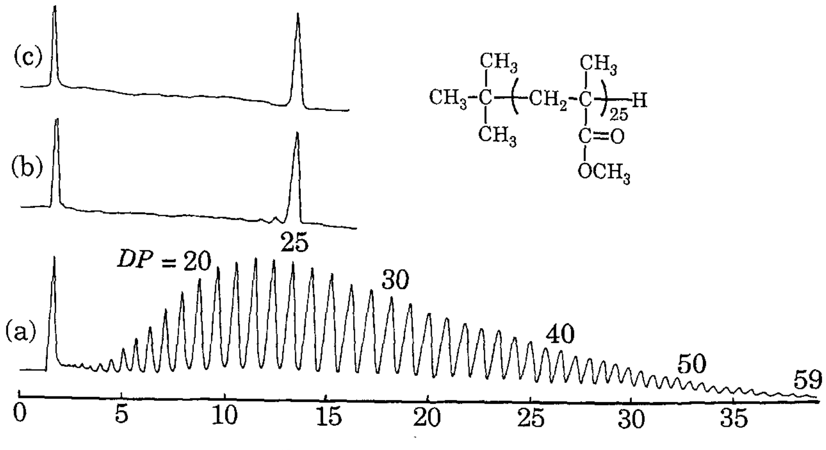

Figure 1. SFC traces of the *it*-PMMA ($\overline{DP}$ = 28.6, $\overline{Mw}/\overline{Mn}$ = 1.15) (a), the crude 25-mer isolated from the PMMA (b) and the 25-mer purified by the repeated fractionation of (b) (c).

25-mer thus obtained was analyzed by the SFC under the same conditions (Figure 1b). The fraction showed an elution peak at the original position, accompanied by some small peaks due to the lower *DP* components. Then, the fraction was subjected to the SFC again, and the pure component giving a single peak in the chromatogram could be isolated (Figure 1c). In a similar manner, several tens or hundreds milligrams of the pure oligomers from 19-mer to 28-mer were obtained, individually.

An SFC curve of the *st*-PMMA ($\overline{DP}$ = 26.8, $\overline{Mw}/\overline{Mn}$ = 1.09) prepared with $t\text{-}C_4H_9Li/(n\text{-}C_4H_9)_3Al$ complex is shown in Figure 2a. The *st*-PMMA was dissolved in acetone at 50 w/v% concentration and the volume of the solution injected on the column was 60 μl. When the larger amount of the sample was used, separation of the elution peaks became poorer, obviously showing a sign of overload. The maximum sample-load for the *st*-PMMA was smaller than that for the *it*-PMMA though the *DP* values of both PMMAs were nearly equal. It seemed that the maximum sample-load was controlled not only by a total amount of the oligomer mixture but also by the amount of the most abundant oligomer component. Because the *st*-PMMA obtained as a hexane-insoluble part has a narrower MWD than the *it*-PMMA, a relative amount of the most abundant compornent in the *st*-PMMA is larger than that in the *it*-PMMA. The pure oligomer fractions from 22-mer to 29-mer were isolated by the SFC-fractionation according to the procedure described for *it*-oligomers (cf. Figures 2b and 2c).

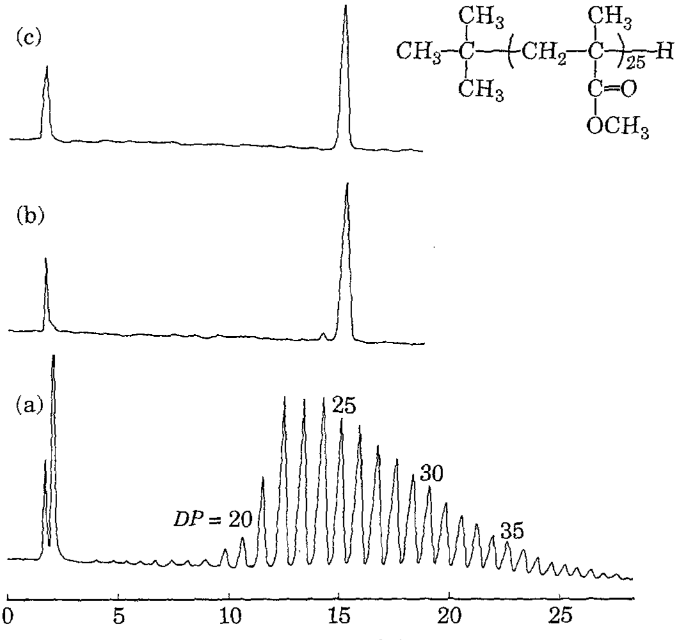

Figure 2. SFC traces of the *st*-PMMA ($\overline{DP}$ = 26.8, $\overline{Mw}/\overline{Mn}$ = 1.09) (a), the crude 25-mer isolated from the PMMA (b) and the 25-mer purified by the repeated fractionation of (b) (c).

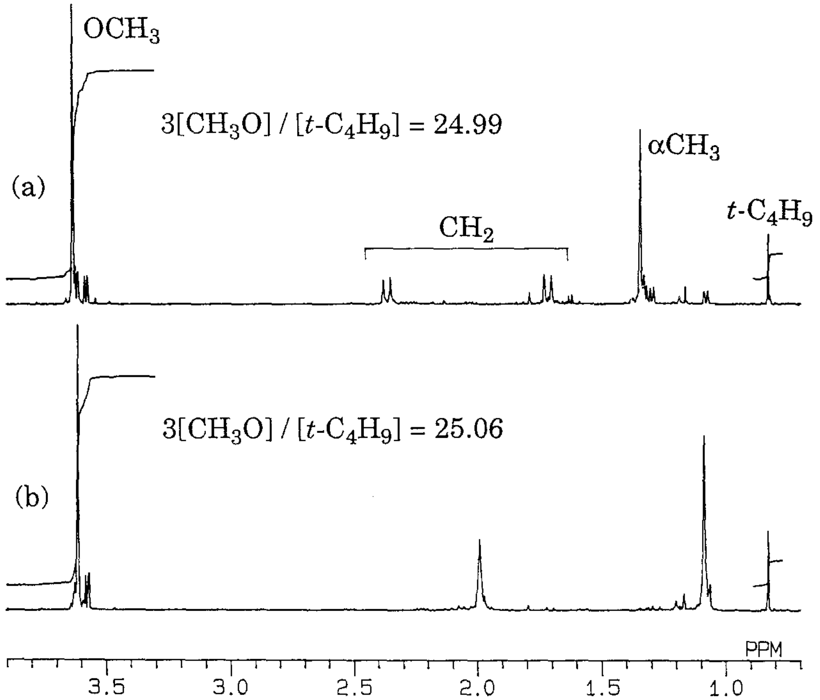

Figure 3. ^1H NMR spectra of the *it*- (a) and *st*-25-mers of MMA (b). (500MHz, nitrobenezne-d_5, 110°C).

An FD mass spectrum of the fraction of *it*-19-mer showed the parent peak at $m/Z = 1959$, indicating that *DP* of the fraction was exactly 19. The fraction of *st*-22-mer exhibited a fragment peak at $m/Z = 2201$, which corresponds to the molecular ion of the 22-mer without the terminal t-C_4H_9-group. The parent peak was hardly detected in the mass spectra of the 20-mers and the higher oligomers. ^1H NMR spectra of the oligomer fractions of *it*- and *st*-25-mers clearly showed that both fractions contained little impurity (Figures 3a and 3b). *DP* of both oligomers was determined as 25 from the intensity ratio of the NMR signals due to the CH_3O- and the terminal t-C_4H_9-groups. The *DP* values are consistent with those determined by the FD mass spectroscopy.

^{13}C NMR measurements of *it*-25-mer and *st*-22-mer gave the spectra of a good signal-to-noise ratio by overnight (12~13 h) measurements as shown in Figure 4. The assignment of the signals was based on that of the *it*- and *st*-octamers [4]. The numbering system for the monomeric units in the oligomers is displayed in the figure. The ^{13}C signals due to α_1-, α_2-, ω_1- and ω_2-monomeric units appered apart from the other signals. On the other hand, the ^{13}C signals of the monomeric units in the third and farther positions from the chain-ends resonated at nearly the same positions as those of high molecular weight *it*- or *st*-PMMA.

A 2 : 1 mixture of *it*- and *st*-24-mers was subjected to the SFC analysis

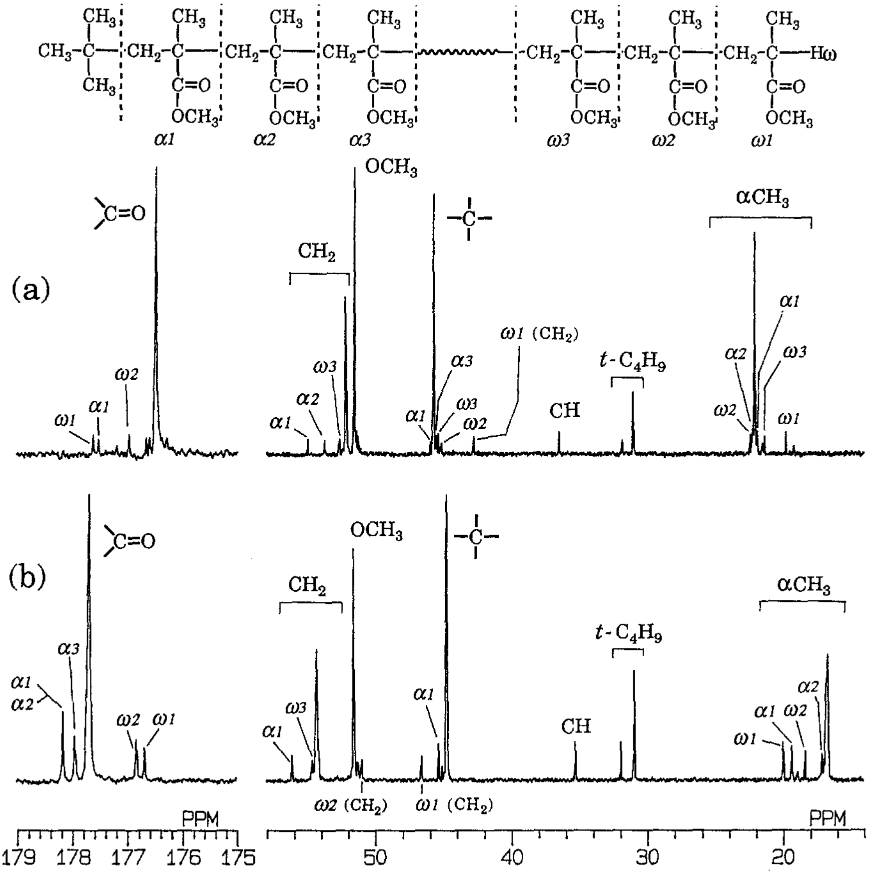

Figure 4. ^{13}C NMR spectra of the *it*- (a) and *st*-25-mers of MMA (b) (125MHz, chloroform-*d*, 55°C).

(Figure 5c). The chromatogram showed two peaks with an intensity ratio of 2 : 1, indicating that the former peak is attributed to the *it*-24-mer and the latter to the *st*-24-mer. The *it*-oligomers eluted faster than the *st*-oligomers also in the separation of the MMA oligomers from the dimer to octamer using the normal phase HPLC [4,5,12]. On the other hand, the *st*-oligomers eluted faster than the *it*-oligomers in the reverse phase SFC analysis using an ODS column [10]. These indicate that *it*-oligomers of MMA have a smaller polarity than *st*-oligomers. Thus SFC was found to be effective also for the separation of stereoisomers of the oligomers. If the SFC experiment of less tactic MMA oligomers without MWD is performed under appropriate conditions, it would be possible to separate some stereoisomers other than the purely *it*- and purely *st*-isomers.

Thermal analysis of the oligomers by DSC

Studies on the physical properties of the stereoregular MMA oligomers without MWD are of great significance. Though the purely isotactic

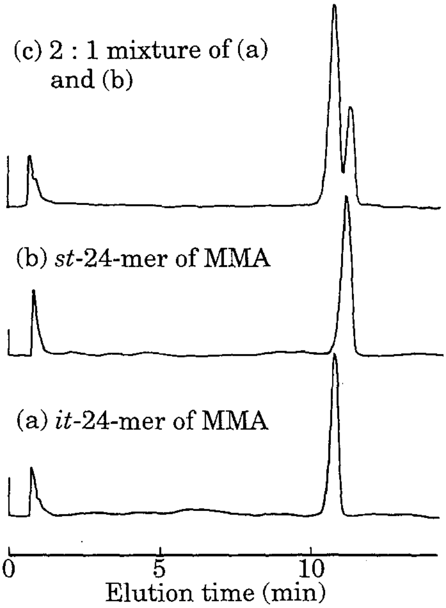

Figure 5. SFC traces of the *it*- (a) and *st*-24-mers of MMA (b) and of a 2 : 1 mixture of the *it*- and *st*-24-mers (c). Mobile phase: CO_2 2.3 ml/min, C_2H_5OH 0.6 ml/min; column: silica gel, 4.6 mm *i.d.* x 150 mm; column temp: 115°C ⟶ 40°C; press.: 202 kgf/cm^2.

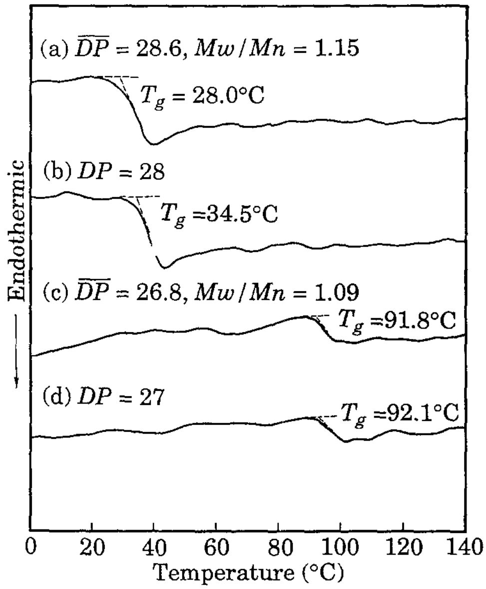

Figure 6. DSC curves of the *it*-PMMA ($\overline{DP}$ = 28.6) (a), the *it*-28-mer (b), the *st*-PMMA ($\overline{DP}$ = 26.8) (c) and the *st*-27-mer (d) (heating rate 10°C/min).

pentamer and the purely syndiotactic tetramer gave single crystals suitable for X-ray analysis [5], the pure *it*- and *st*-19- to 29-mers isolated in this work were rather amorphous.

DSC analysis of the *it*-28-mer showed a glass transition (T_g) at 34.5°C (Figure 6b). The value was higher by 6.5°C than the T_g of the *it*-PMMA which had $\overline{DP}$ of nearly equivalent value (28.6) (Figure 6a). The lower T_g of the *it*-PMMA may be ascribed to the plasticizing or solvating effect of the lower *DP* components existing in the *it*-PMMA. On the other hand, little difference was observed between the T_g values of *st*-27-mer and *st*-PMMA ($\overline{DP}$ = 26.8) (Figures 6c and 6d), probably because of the fact that the *st*-PMMA contains the lower *DP* components in a smaller amount. T_g of both the *it*- and *st*-oligomers from 22-mer to 29-mer increased linearly with *DP*, and the T_g of the *st*-oligomer was higher than the corresponding *it*-oligomer (Figure 7).

It has been known that *it*- and *st*-PMMA chains associate to form a crystalline stereocomplex under certain conditions [13,14]. A 1 : 1 mixture of the *it*- and *st*-27-mers showed a sharp DSC endothermic transition at 102.3°C which was attributable to melting of the stereocomplex (Figure 8b). This mixture was prepared by the evaporation of the acetone solution with nitrogen flow and the subsequent annealing at 140°C for 15h. A 1 : 1 mixture of the *it*- and the *st*-PMMAs prepared in a similar manner had a much broader

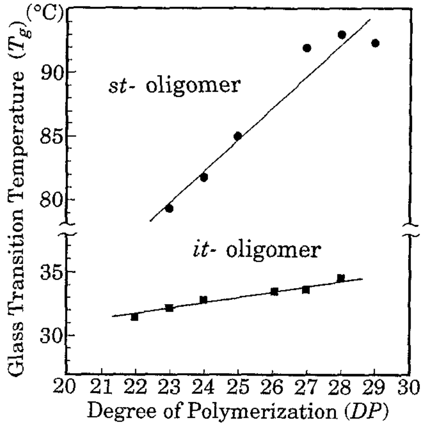

Figure 7. Relation between *DP* and T_g for the *it*- and *st*-oligomers of MMA.

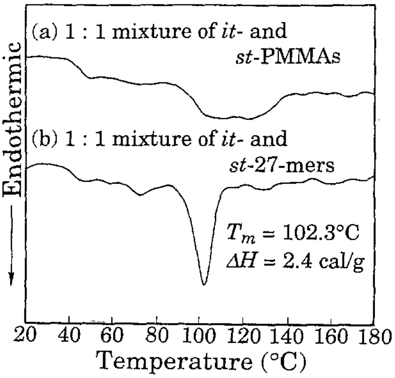

Figure 8. DSC curves of a 1:1 mixture of the *it*- and *st*-PMMA(a) and of the *it*-and *st*-27-mers of MMA (b) (heating rate 10°C/min).

endotherm around 80 ~ 140°C (Figure 8a). This suggests that the *it*- and *st*-oligomers without MWD form a stereocomplex having much ordered structure than those with MWD.

REFERENCES

1. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
2. T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, K. Hatada, *Makromol. Chem., Suppl.*, **15**, 167 (1989).
3. Y. Okamoto, E. Yashima, T. Nakano, K. Hatada, *Chem. Lett.*, 759 (1987).
4. K. Ute, T. Nishimura, K. Hatada, *Polym. J.*, **21**, 1027 (1989).
5. K. Ute, N. Miyatake, K. Hatada, *J. Macromol. Sci.-Chem.*, **A29**, (1992), in press.
6. R. E. Jentoft, T. H. Gouw, *J. Polym. Sci.*, **B7**, 811 (1969).
7. F. P. Schmitz, E. Klesper, *J. Supercrit. Fluids*, **3**, 29 (1990), and the references therein.
8. W. Hartmann, E. Klesper, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 713 (1977).
9. E. Klesper, W. Hartmann, *Eur. Polym. J.*, **14**, 77 (1978).
10. K. Hatada, K. Ute, T. Nishimura, M. Kashiyama, T. Saito, M. Takeuchi, *Polym. Bull.*, **23**, 157 (1990).
11. K. Ute, T. Asada, N. Miyatake, K. Hatada, *Makromol. Chem., Macromol. Symp.*, to be submitted.
12. K. Hatada, K. Ute, K. Tanaka, M. Imanari, N. Fujii, *Polym. J.*, **19**, 425 (1987).
13. A. M. Liquori, G. Anzuino, V. M. Corio, M. D'Alagni, P. de Santis, A. Savino, *Nature*, **206**, 358 (1965).
14. E. L. Feitsma, A. de Boer, G. Challa, *Polymer*, **16**, 515 (1975).

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