5102 *Macromolecules* **1990,** *23,* 5102-5105

# Dilute Solution Properties of Semiflexible Poly(substituted methylenes): Intrinsic Viscosity of Poly(diisopropyl fumarate) in Benzene

**Akikazu Matsumoto, Tetsuya Tarui, and Takayuki Otsu***

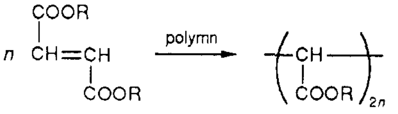
*Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan*

*Received March 12, 1990; Revised Manuscript Received May 10, 1990*

ABSTRACT: The relationship between intrinsic viscosity ([$\eta$]) and molecular weight ($\bar{M}$) was determined for poly(diisopropyl fumarate) (poly(DiPF)) prepared by radical polymerization and then fractionated; [$\eta$] = $7.53 \times 10^{-6}\bar{M}^{0.98}$ (dL/g) (in benzene at 30 °C, $\bar{M} < 3 \times 10^5$). The index number ($a$ = 0.98) is the largest among the values reported for vinyl polymers, indicating that poly(DiPF) has a considerably rigid (semiflexible) conformation because of the poly(substituted methylene) structure with bulky side groups. The $a$ value decreases continuously from 0.98 to ca. 0.8 with increasing molecular weight. The value depends on the ester alkyl group; i.e., it was determined to be 0.87 for poly(diethyl fumarate) (poly(DEF)), suggesting that flexibility of the poly(DiPF) chain is less than that of poly(DEF). From GPC measurement of these poly(dialkyl fumarates), the flexibility of the chains was compared. Furthermore, estimation of the persistence length for poly(DiPF) in benzene was attempted from the viscosity data.

## Introduction

In previous papers,[1-6] it has been reported that dialkyl fumarates (DRF) can polymerize easily in the presence of a radical initiator and that the introduction of bulky alkyl esters increases their polymerization reactivities (both polymerization rate and molecular weight of the resulting polymers), although 1,2-disubstituted ethylenes have been generally recognized to polymerize only with difficulty because of steric hindrance in propagation. It was confirmed that the polymerization proceeded via opening of their double bonds, i.e., by the ordinary vinyl polymerization mechanism to give poly[(alkoxycarbonyl)methylenes] (eq 1).



$$n\ \overset{\mathrm{COOR}}{\overset{|}{\mathrm{CH}}}=\underset{\underset{\mathrm{COOR}}{|}}{\mathrm{CH}} \xrightarrow{\text{polymn}} \left(\underset{\underset{\mathrm{COOR}}{|}}{\mathrm{CH}}\right)_{2n} \qquad (1)$$

These poly(substituted methylenes) have no methylene group ($CH_2$) as a spacer in their main chains, and their backbones are surrounded closely with the side chains. As a result, poly(substituted methylenes) have a more rigid conformation, due to bulkiness of the substituents, as distinguished from ordinary vinyl polymers, i.e., poly(substituted ethylene). As one of the specific properties of the poly(substituted methylenes), the formation of semiflexible polymer chains with bulky substituents might lead to a decrease in the rate of mutual termination in radical polymerization, resulting in enhancement of apparent polymerization reactivities of DRF with an ester group such as diisopropyl fumarate (DiPF) or di-*tert*-butyl fumarate (DtBF).[2-6] We have already suggested that poly(DiPF)[3] and poly(DtBF)[2] have relatively low flexibility, based on consideration of their molecular models. Moreover, the Mark-Houwink-Sakurada viscosity-molecular weight relation was examined with respect to unfractionated samples ($\bar{M}_w/\bar{M}_n$ = 1.9-2.1) of poly(DiPF) in toluene.[3]

A few semiflexible wormlike chains have been intensively investigated,[7] e.g., polyamides,[8-11] cellulose derivatives,[12,13] DNA,[12,14] and polysaccharides.[15,16] In general, very few typical stiff chains are found among vinyl polymers, for which the structure of repeat units, molecular weight and its distribution, and configurations are capable of being controlled by polymerization conditions.[17,18] Poly(*tert*-butyl crotonate) (poly(TBC)) has been studied since 1974 by Nagasawa and *co*-workers as an apparently unique example of a semiflexible vinyl polymer; i.e., poly(TBC) with a semiflexible backbone and narrow molecular weight distribution was prepared by living anionic polymerization[19] and characterized as to the rigidity of the polymer chain.[20,21]

We have been interested in the steric effects in DRF which increase the polymerization reactivities, as mentioned above, whereas steric hindrance in general may also cause a reduction of reactivity. Therefore we have undertaken the characterization of semiflexible wormlike polymethylene derivatives from DRF in dilute solution.

## Experimental Section

**Preparation of Polymers.** DiPF and diethyl fumarate (DEF) were prepared as reported previously.[1-6] Other reagents and solvents were purified by ordinary methods. Polymerization of DRF was carried out in a sealed glass tube in the presence of 2,2′-azobis(isobutyronitrile) or benzoyl peroxide. Polymerization of DiPF was performed in bulk at 30 or 50 °C and in benzene at 70 °C in order to obtain polymers with different molecular weights. DEF was polymerized in bulk at 30 or 60 °C. The effect of solvents, initiators, and temperature on tacticity of the polymers was neglected, especially in the case of poly(DiPF).[22] After polymerization for a given time, the polymerization mixture in the tube was poured into a large amount of methanol or *n*-hexane to isolate the resulting polymer. The polymer was filtered, washed, and then dried under vacuum at room temperature for 1 day. The polymer was purified by reprecipitation from benzene and methanol or *n*-hexane.

**Fractionation.** The precipitation-fractionation of poly(DiPF) was carried out with tetrahydrofuran (THF) as a solvent and methanol as a nonsolvent at 30 °C. The results for fractionation of poly(DiPF) prepared by bulk polymerization at 50 °C are shown in Table I. Poly(DEF) was fractionated similarly with THF and water.

**Measurements.** The viscosity of the polymers was measured with an Ubbelohde viscometer in benzene at 30 °C. Intrinsic viscosity ([$\eta$]) was determined by extrapolation to $c = 0$ in both plots of $\eta_{sp}/c$ and $(\ln \eta_{rel})/c$ against $c$, where $c$ is concentration of the polymer and $\eta_{sp}$ and $\eta_{rel}$ are specific and relative viscosities, respectively. Number-average molecular weights ($\bar{M}_n$) of the polymers were determined by membrane osmometry (Knauer) in toluene at 36 °C. $\bar{M}_n$ and second virial coefficients were determined by plots of $\pi/c$ against $c$, where $\pi$ is osmotic pressure.

0024-9297/90/2223-5102$02.50/0 © 1990 American Chemical Society

Table I
Results of Fractionation and Molecular Weight Determination of Poly(diisopropyl fumarate)[a]

| | | | viscosity[b] | | GPC[c] | | OS[d] | | |
|---|---|---|---|---|---|---|---|---|---|
| no. | yield, g | cumulative, % | [$\eta$], dL/g | Huggins const, $k'$ | $\bar{M}_{n,GPC} \times 10^{-4}$ | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_n \times 10^{-4}$ | $A_2 \times 10^4$, mL/g$^2$ | $\bar{M}_{cor} \times 10^{-4}$ |
| 1 | 0.571 | 5.4 | 1.82 | 0.53 | 43.3 | 2.11 | | | |
| 2 | 0.664 | 11.6 | 2.31 | 0.55 | 58.3 | 1.37 | 36.5 | 3.74 | 50.0 |
| 3 | 0.510 | 16.5 | 1.77 | 0.52 | 43.2 | 1.37 | | | |
| 4 | 0.454 | 20.7 | 1.75 | 0.51 | 44.9 | 1.34 | | | |
| 5 | 0.476 | 25.2 | 1.65 | 0.51 | 41.5 | 1.30 | 34.4 | 4.00 | 44.7 |
| 6 | 0.703 | 31.9 | 1.68 | 0.61 | 41.8 | 1.25 | 28.0 | 4.44 | 35.0 |
| 7 | 0.430 | 35.9 | 1.45 | 0.50 | 36.8 | 1.27 | 24.1 | | 30.6 |
| 8 | 0.795 | 43.4 | 1.35 | 0.50 | 35.6 | 1.21 | 20.9 | | 25.3 |
| 9 | 0.440 | 47.5 | 1.34 | 0.49 | 38.1 | 1.20 | 21.1 | 4.71 | 25.3 |
| 10 | 0.523 | 52.5 | 1.34 | 0.48 | 34.3 | 1.17 | | | |
| 11 | 0.598 | 58.1 | 1.15 | 0.50 | 28.8 | 1.18 | 19.3 | 4.37 | 22.8 |
| 12 | 0.564 | 63.4 | 1.07 | 0.48 | 27.5 | 1.18 | 16.4 | 4.45 | 19.4 |
| 13 | 0.450 | 67.7 | 0.958 | 0.48 | 24.0 | 1.19 | 15.9 | 4.83 | 18.9 |
| 14 | 0.509 | 72.5 | 0.934 | 0.50 | 23.1 | 1.24 | 14.9 | 4.57 | 18.5 |
| 15 | 0.667 | 78.8 | 0.896 | 0.52 | 21.4 | 1.24 | 13.4 | 4.59 | 16.6 |
| 16 | 0.683 | 85.2 | 0.832 | 0.52 | 17.5 | 1.24 | 11.7 | 6.32 | 14.5 |
| 17 | 0.773 | 92.5 | 0.651 | 0.56 | | | | | |
| 18 | 0.521 | 97.4 | 0.477 | 0.57 | 8.39 | 1.36 | 7.63 | 5.83 | 10.4 |
| 19 | 0.277 | 100.0 | 0.289 | 0.55 | 5.13 | 1.26 | 3.74 | 5.80 | 4.71 |

[a] Polymerized in bulk with 2,2′-azobis(isobutyronitrile) (0.02 mol/L) at 50 °C for 50 h; polymer yield 49.4%, [$\eta$] = 1.13 dL/g, $\bar{M}_w/\bar{M}_n = 2.22$. [b] In benzene at 30 °C. [c] Gel permeation chromatography calibrated with standard polystyrenes in THF at 38 °C. [d] Membrane osmometry in toluene at 36 °C. $\bar{M}_{cor}$ was calculated with $\bar{M}_n$(OS) and $\bar{M}_w/\bar{M}_n$(GPC).

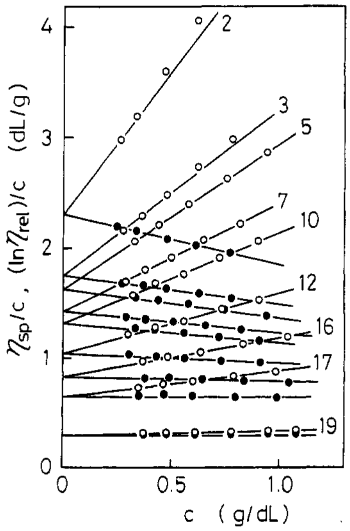


**Figure 1.** Plots of $\eta_{sp}/c$ (○) and $(\ln \eta_{rel})/c$ (●) against $c$ for poly(diisopropyl fumarate) in benzene at 30 °C. The numbers indicate the fraction numbers in Table I.

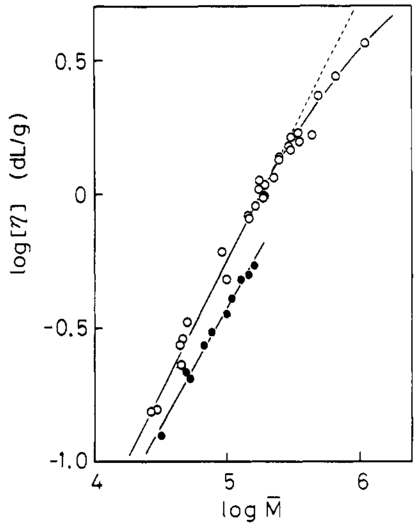


**Figure 2.** Relationship between [$\eta$] and $\bar{M}$ of poly(diisopropyl fumarate) (○) and poly(diethyl fumarate) (●) in benzene at 30 °C.

Gel permeation chromatography (GPC) was carried out in THF at 38 °C (Tosoh 8000 Series GPC systems with columns; TSK-gel G6000HXL, G4000HXL × 2, G2000HXL) and calibrated with standard polystyrenes (Tosoh). Weight-average molecular weights ($\bar{M}_{cor}$) were calculated by combination of $\bar{M}_n$ by osmometry and $\bar{M}_w/\bar{M}_n$ by GPC. $\bar{M}_{cor}$ was used for determinations of viscosity equation parameters and persistence length, instead of the viscosity-average molecular weight ($\bar{M}_v$) (see text).

## Results and Discussion

Table I shows the results of the fractionation of a poly(DiPF) obtained by radical polymerization in bulk at 50 °C. This sample was divided into 19 fractions. The results of viscosity, GPC, and osmotic pressure measurements of each fraction are also shown in Table I. The GPC data indicate that all the fractions have a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.3$). In Figure 1, typical plots for the determination of [$\eta$] are shown. The values of [$\eta$] in benzene at 30 °C were in the range 0.3–2.3 dL/g. Huggins constants were 0.5–0.6, which are somewhat larger than values expected for linear and flexible polymers in a good solvent.[23] The $\bar{M}_n$ values determined osmometrically were found to be from $3.7 \times 10^4$ to $37 \times 10^4$, and $A_2$ increased from $4 \times 10^{-4}$ to $6 \times 10^{-4}$ mL/g$^2$ when $\bar{M}_n$ decreased.

For evaluation of the viscosity–molecular weight relation, $\bar{M}_v$ should be used because the fractionated poly(DiPF) samples in this work have relatively narrow molecular weight distributions but are not monodisperse. In this case, the viscosity is nearly proportional to the molecular weight ($a \sim 1$) as described later, so that $\bar{M}_v$ is close to $\bar{M}_w$. Therefore, we used a corrected molecular weight ($\bar{M}_{cor}$), which is calculated by combination of $\bar{M}_n$ by osmometry and $\bar{M}_w/\bar{M}_n$ by GPC, instead of $\bar{M}_v$. The $\bar{M}_{cor}$ calculated are shown in Table I.

The relation between [$\eta$] and $\bar{M}$ is shown in Figure 2, which includes results for other polymerized and fractionated poly(DiPF), i.e., higher molecular weight fractions ($1.5 \times 10^5 < \bar{M} < 1.1 \times 10^6$) from bulk polymerization at 30 °C and a lower molecular weight fraction ($\bar{M} < 4.6 \times 10^4$) from polymerization in benzene at 70 °C. The plot for [$\eta$] of poly(DiPF) in the range of $\bar{M}$ from $10^4$ to $10^6$ gives a curve with moderately convex-upward bending; i.e., the slope of the experimental curve continuously decreases from 0.98 to ca. 0.8 as $\bar{M}$ increases from $10^4$ to $10^6$. In the region below $\bar{M} = 3 \times 10^5$, the relation between $[\eta]$ and $\bar{M}$ is approximated as

$$[\eta] = 7.53 \times 10^{-6}\bar{M}^{0.98} \quad \text{(in benzene at 30 °C)} \qquad (2)$$

where $[\eta]$ is in dL/g.

The index number $a$ in this equation is the largest among the values reported for vinyl polymers.[24] The high $a$ value (0.98) for poly(DiPF) is similar to those for semiflexible cellulose derivatives, polyamides, and polyimides. Among vinyl polymers, only the unique example of poly(*tert*-butyl crotonate) (poly(TBC)) has been reported ($a = 0.96$ in toluene at 25 °C).[19] The $a$ value for poly(DiPF) obtained in this work is thus close to that for poly(TCB). In the high molecular weight region in Figure 2, a deviation from the relation represented with eq 2 was observed as mentioned above. It may indicate that the flexibility of the poly(DiPF) chain changes depending on the chain length. It has been reported that other semiflexible polymers have such a curve in a log $[\eta]$–log $M$ relation.[11,19]

The maximum $a$ value for a flexible random coil is 0.8 as a theoretically predicted limiting one in a good solvent, and the actual experimental values are lower than that even in the high molecular weight region.[25] Moreover, it is obvious that the $[\eta]$ values for poly(DiPF) are higher than those for random coils from ordinary flexible vinyl polymers bearing a corresponding $\bar{M}$, e.g., not only polystyrene in cyclohexane at 34.5 °C as a Θ solvent ($[\eta] = 8.8 \times 10^{-4}\bar{M}_w^{0.50}$),[26] but also polystyrene in benzene as a good solvent ($[\eta] = 7.8 \times 10^{-5}\bar{M}_w^{0.75}$)[26] and poly(methyl methacrylate) in acetone ($[\eta] = 5.7 \times 10^{-5}\bar{M}_w^{0.70}$).[27] This supports the conclusion that the poly(DiPF) chain has a considerably extended conformation in benzene because of its intrinsic semiflexibility.

In Figure 2, a similar relation for poly(diethyl fumarate) (poly(DEF)), which was prepared in bulk polymerization followed by fractionation ($\bar{M}_w/\bar{M}_n = 1.2$–$1.5$), is also included. From these plots, the constants for poly(DEF) in the viscosity–molecular weight equation were determined in the range of $\bar{M}$ below $2 \times 10^5$ as shown in eq 3:

$$[\eta] = 1.62 \times 10^{-5}\bar{M}^{0.87} \quad \text{(in benzene at 30 °C)} \qquad (3)$$

The $a$ value for poly(DEF) was smaller than 0.98 for poly(DiPF), and the plots for $[\eta]$ values for poly(DEF) were always situated below those for poly(DiPF) with an identical $\bar{M}$, indicating that the rigidity of the chain decreased in poly(DEF). This decrease in the flexibility of the poly(DRF) chain sensitively depending on the bulkiness of the ester groups is assumed to originate from the poly(substituted methylene) structure, and it also influences significantly the properties of the polymers in bulk.[6,28,29]

As shown in Table I, $\bar{M}_n$ determined by GPC is always higher than its absolute value, i.e., $\bar{M}_n$ determined by the osmometric measurement, because the former was calibrated with standard polystyrenes, which are typical flexible polymers. In Figure 3, the relation between $\bar{M}_n$ and elution volume ($V_e$) is shown. It was found that both poly(DRF)s eluted at smaller volumes than polystyrene. Since polystyrene is considered to be well extended in THF as a good solvent, this suggests that the expansion of the semiflexible poly(DRF) is considerably large. Moreover, $V_e$ for poly(DiPF) is smaller than for poly(DEF), in agreement with the results of the viscosity measurements in benzene.

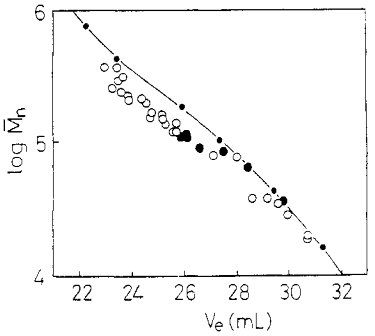


**Figure 3.** Relationship between $\bar{M}_n$ and elution volume ($V_e$) for GPC in THF at 38 °C: (○) poly(diisopropyl fumarate); (●) poly(diethyl fumarate); (– • –) polystyrene.

We attempted to estimate the persistence length ($q$) of the poly(DiPF) chain in benzene from the viscosity data above, in accordance with the relationship between intrinsic viscosity and molecular weight in the following equations:[12]

For $L/2q \geq 2.278$

$$[\eta] = \Phi_\infty M^{1/2}(M_L/2q)^{-3/2}[1 - (\sum_{i=1}^{4} C_i(L/2q)^{-i/2})]^{-1} \qquad (4)$$

where $\Phi_\infty$ is the Flory–Fox constant ($2.87 \times 10^{23}$ in cgs units), $L$ is the contour length of the chain, $M_L$ is the molar mass per unit contour length (i.e., $L = M/M_L$), and $C_i$ are coefficients depending on the values of the diameter ($d$) of the cylinder and $q$.

For $L/2q < 2.278$

$$[\eta] = \frac{\pi N_A L^3}{24M \ln (L/d)} \frac{f(L,q)}{1 + \sum_{i=0}^{4} A_i[\ln (d/L)]^{-i}} \qquad (5)$$

where $N_A$ is Avogadro's number, $f(L,q)$ is a function depending on $L$ and $q$, and $A_i$ are constants independent of $L$, $d$, and $q$.

The approximation of Bohdanecký[30] (eq 6) was adapted for unequivocal estimation of $M_L$ and $q$ for poly(DiPF).

$$(\bar{M}^2/[\eta])^{1/3} = A_\eta + B_\eta \bar{M}^{1/2} \qquad (6)$$

with

$$A_\eta = \Phi_\infty^{-1/3} A_0 M_L \qquad (7)$$

$$B_\eta = \Phi_\infty^{-1/3} B_0 (M_L/2q)^{1/2} \qquad (8)$$

where $A_0$ and $B_0$ are functions of $d/2q$ as represented in the following equations, respectively:[30]

$$A_0 = 0.46 - 0.53 \log (d/2q) \qquad (9)$$

$$B_0 = 1.00 - 0.0367 \log (d/2q) \qquad (10)$$

Figure 4 shows the plot of $(\bar{M}^2/[\eta])^{1/3}$ versus $\bar{M}^{1/2}$ for poly(DiPF). A straight line having intercept and slope 153 and 1.27 $g^{1/3}\cdot cm^{-1}$, respectively, was obtained. From these values and the Flory–Fox constant, $A_0 M_L = 1.01 \times 10^{10}$ cm$^{-1}$ and $B_0(M_L/2q)^{1/2} = 8.40 \times 10^7$ cm$^{-1}$ are given. These values yield $M_L = 1000$ nm$^{-1}$ and $q = 7.6$ nm for $d = 1.4$ nm.[6,28] The comparison between the experimental $[\eta]$ values and theoretical values is depicted in Figure 5, indicating good agreement with each other.

The $q$ value determined is the largest so far reported for a vinyl polymer.[7] It is also larger than that estimated for semiflexible poly(TBC) (5–6 nm from light scattering[19] and viscosity[20] and 2–3 nm from small-angle X-ray scattering[21]). This is reasonable from the difference in the

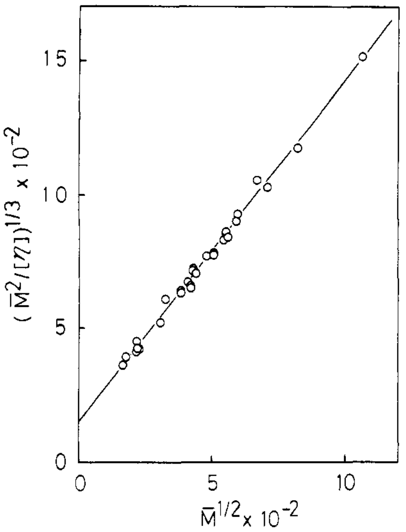


**Figure 4.** Plot of $(\bar{M}^2/[\eta])^{1/3}$ against $\bar{M}^{1/2}$ for poly(isopropyl fumarate).

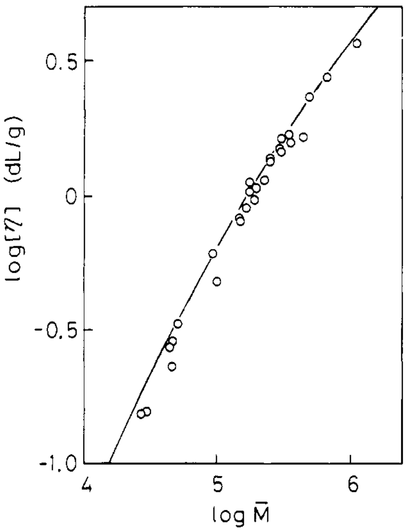


**Figure 5.** Comparison between the experimental data (○) of the intrinsic viscosity for poly(diisopropyl fumarate) in benzene at 30 °C and the calculated values (the solid line) from eqs 4 and 5 with $M_L$ = 1000 nm$^{-1}$, $q$ = 7.6 nm, and $d$ = 1.4 nm.

bulkiness of the β-substituent, i.e., an alkoxycarbonyl group in poly(DRF) and a methyl group in poly(TBC).

Light scattering from THF solutions of poly(DiPF) can be used to determine the radius of gyration of the chain, but the intensity of scattering from benzene solutions is insufficient for this purpose. A comparison of the $q$ value obtained in this work with that calculated from the radius of gyration will be reported in the future.

**Acknowledgment.** We thank Mr. Takashi Yasuhara for viscosity measurements. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 01430019) from the Ministry of Education, Science and Culture, Japan.

## References and Notes

(1) Otsu, T.; Ito, O.; Toyoda, N.; Mori, S. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 725.
(2) Otsu, T.; Yasuhara, T.; Shiraishi, K.; Mori, S. *Polym. Bull.* **1984**, *12*, 449.
(3) Otsu, T.; Minai, H.; Toyoda, N.; Yasuhara, T. *Makromol. Chem., Suppl.* **1985**, *12*, 133.
(4) Otsu, T.; Shiraishi, K. *Macromolecules* **1985**, *18*, 1795.
(5) Otsu, T. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 235.
(6) Otsu, T.; Yasuhara, T.; Matsumoto, A. *J. Macromol. Sci.—Chem.* **1988**, *A25*, 537.
(7) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23 and references therein.
(8) Sadanobu, J.; Norisuye, T.; Fujita, H. *Polym. J.* **1981**, *13*, 75.
(9) Berger, M. N. *J. Macromol. Sci.—Rev.* **1973**, *C9*, 269.
(10) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727.
(11) Murakami, H.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 345. Kuwata, M.; Murakami, H.; Norisuye, T.; Fujita, H. *Ibid.* **1984**, *17*, 2731.
(12) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128. Yamakawa, H.; Yoshizaki, T. *Ibid.* **1980**, *13*, 633.
(13) Penzel, E.; Schulz, G. V. *Makromol. Chem.* **1968**, *113*, 64.
(14) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 649.
(15) Kashiwagi, Y.; Norisuye, T.; Fujita, H. *Macromolecules* **1981**, *14*, 1220.
(16) Sato, T.; Norisuye, T.; Fujita, H. *Polym. J.* **1984**, *16*, 341; *Macromolecules* **1984**, *17*, 2696.
(17) Mays, J. W.; Hadjichristidis, N. *J. Macromol. Sci.—Rev.* **1988**, *C28*, 371. Saikali-Kioulafa, E.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1989**, *22*, 2059.
(18) Tricot, M. *Macromolecules* **1986**, *19*, 1268.
(19) Kitano, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1974**, *7*, 719.
(20) Noda, I.; Imai, T.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 1303. Noda, I.; Yamamoto, Y.; Kitano, T.; Nagasawa, M. *Ibid.* **1981**, *14*, 1306.
(21) Muroga, Y.; Sakuragi, I.; Noda, I.; Nagasawa, M. *Macromolecules* **1984**, *17*, 1844.
(22) Yoshioka, M.; Matsumoto, A.; Otsu, T., in preparation.
(23) Yamakawa, H. *J. Chem. Phys.* **1961**, *34*, 1360.
(24) Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; p IV-1.
(25) Fujita, H. *Macromolecules* **1988**, *21*, 179.
(26) Einaga, Y.; Miyaki, Y.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2103.
(27) Kashiwagi, Y.; Einaga, Y.; Fujita, H. *Polym. J.* **1980**, *12*, 271.
(28) Yamada, K.; Takayanagi, M.; Murata, Y. *Polymer* **1986**, *27*, 1054.
(29) Choi, S. B.; Takahara, A.; Amaya, N.; Murata, Y.; Kajiyama, T. *Polym. J.* **1989**, *21*, 215, 433.
(30) Bohdanecký, M. *Macromolecules* **1983**, *16*, 1483.