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Conformational Studies on an Optically Active 1,4-Polyketone in Solution

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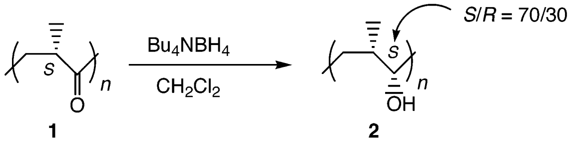
ABSTRACT: Conformation of a chiral γ-polyketone, poly((*S*)-1-oxo-2-methyltrimethylene) (**1**), in solution was investigated by CD and ORD spectropolarimetry and static light scattering refractometry. Variable-temperature CD and ORD spectra of **1** as compared with that of a chiral diketone (*S*)-3-methyl-2,5-hexanedione (**3**), a model compound of **1**, afforded no evidence of polyketone **1** forming stable helical conformation. Static light scattering refractometry showed M_w value of **1** was 18 800, smaller than M_w 27 600 measured by GPC, indicating the existence of an extended conformation. The number-average root-mean-square radius of gyration $R_{g,n}$ is evaluated to be 9.94 nm by static light scattering.

Introduction

Isotactic polypropylene has a stable helical structure in a solid state.[1] However, when the polymer is dissolved in a solvent, the dynamics of the polymer chain is extremely fast to induce rapid reversal of helicity.[2−4] Another example of isotactic polymer made of propene is optically active α-methyl-γ-polyketone **1** which we synthesized via asymmetric alternating copolymerization of propene and carbon monoxide.[5,6] Polyketone **1** is a perfectly alternating copolymer; its structure is controlled to head-to-tail and isotactic. Since the absolute configuration of the asymmetric carbon atom attached to the carbonyl group in polyketone **1** is controlled to be all *S*-configuration, one may expect that such stereoregularity will induce secondary structure of this polymer; e.g., helical structure.[3] In the crystalline state, the s(2/1) helical conformation was confirmed by powder X-ray diffraction for an optically pure copolymer of styrene and CO.[7,8] Also, in the solid amorphous phase, it is suggested that the optically active methylstyrene/1-decene/CO terpolymer forms a helical structure below T_g.[9] Nevertheless, detailed conformational studies on polyketone **1** have remained unexplored as yet.[6,10]

Previously, we reported the diastereoselective reduction of this polyketone **1** to give polyol **2**.[11] In this case, the newly formed asymmetric center next to the hydroxyl group was controlled to be *S*-configuration to some extent (eq 1). Notably, the *S*-selectivity observed in the polymer reduction contradicts Cram's rule,[12] a well-documented empirical rule about the selectivity for the nucleophilic addition to a carbonyl group bearing α-asymmetric center. Thus, if we assume that polyketone **1** forms a planar zigzag conformation, the hydride would attack from the opposite side of the α-methyl, the result matching the anti-Cram selectivity.



(1)

To evaluate our assumption mentioned above, we carried out the conformational studies on polyketone **1** in solution by variable-temperature circular dichroism (CD), optical rotatory dispersion (ORD), and static light-scattering measurements.

Experimental Section

General Data. Polyketone **1** was prepared by asymmetric alternating copolymerization of propene and carbon monoxide with Pd(II)−*(R,S)*-BINAPHOS catalyst by the procedure of our previous reports.[5] A model diketone, (*S*)-3-methyl-2,5-hexanedione (**3**), was prepared by the reaction of (*S*)-methylsuccinic acid with methyllithium (ether solution) in THF at 25 °C for 24 h and then at 75 °C for 16 h according to the literature method.[11] Most of the reagents were available from Wako Pure Chemical Industries Ltd. or Nacalai Tesque Ltd. All of the solvents used were distilled under argon after drying over an appropriate drying agent. For silica gel column chromatography, Wako-gel C-200 was used.

Molecular weight distribution was detected by size exclusion chromatography (Shodex, KF-804L) using polystyrene as a standard.

CD and ORD Measurements of Polyketone 1 and Diketone 3 at Low Temperatures. Variable temperature CD and simultaneous UV−vis spectra were recorded using a JASCO J-820 spectropolarimeter with a liquid nitrogen-cooled cryostat for temperatures ranging from +23 to −40 °C (0.5 cm path length cell; sample concentration 0.01 mol dm^{-3}).

Variable-temperature ORD spectra were recorded using a JASCO ORDM-401 attached to JASCO J-820 spectropolarimeter with a liquid nitrogen-cooled cryostat for temperatures ranging from +20 to −10 °C (0.1 cm path length cell; sample concentration 0.07 mol dm^{-3}).

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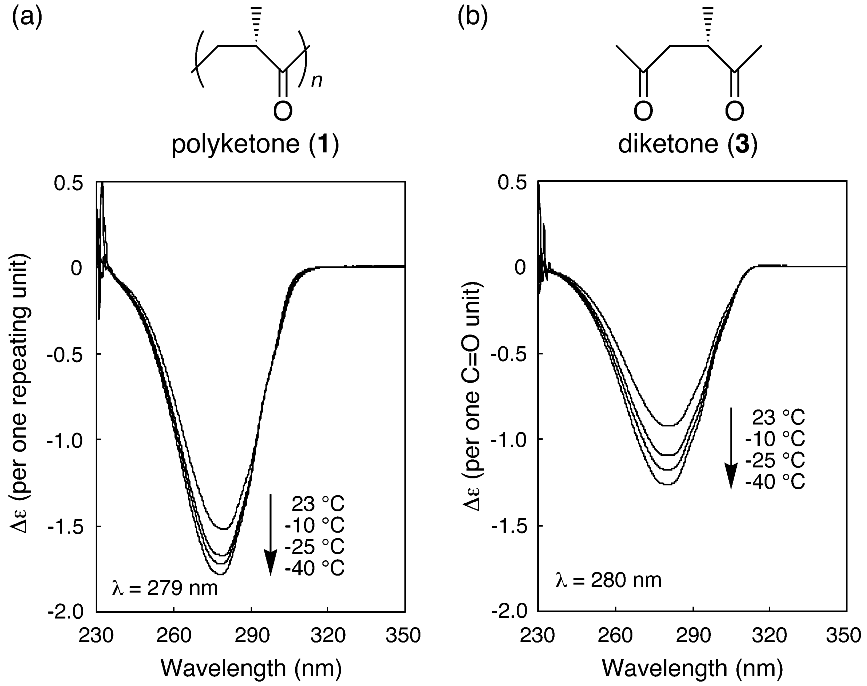

Figure 1. Variable-temperature CD spectra of (a) polyketone **1** (0.01 mol repeating unit per litter) and (b) diketone **3** (0.01 mol of ketones per litter) in chloroform.

Static Light Scattering Measurement of Polyketone 1. Static light scattering measurement of the polyketone in chloroform solution was performed using SLS-5000HM (Otsuka, Ltd.). A vertically polarized light at 632.8 nm line of He−Ne laser was used as the incident light source. The scattered light was recorded in an angular region from 45 to 135° with a 15° difference at a temperature of 25.05 ± 0.05 °C. The sample solution was optically purified by filtration through 0.20 μm Teflon membrane filters and introduced into the light scattering cell. Five solutions of different polyketone concentration of 0.010 to 0.040 g mL^{-1} were prepared. The refractive index increment (dn/dc) of the polyketone solution in chloroform was measured at 25.10 ± 0.02 °C by a DRM-1021 laser differential refractometer (Otsuka, Ltd.) using the He−Ne laser and $\mathrm{d}n/\mathrm{d}c = 0.0508$ mL g^{-1} was obtained.

Weight-average molecular weight M_w, second virial coefficient A_2, and z-average root-mean-square radius of gyration $R_{g,z}$ were determined by the Berry plot

$$(Kc/R_0)^{1/2} = M_w^{-1/2} + A_2 M_w^{1/2} c \qquad (2)$$

$$(Kc/R_\theta)_{c=0}^{1/2} = \frac{1}{M_w^{1/2}}\left(1 + \frac{1}{6}R_{g,z}^{2} q^2\right)$$
$$q^2 = \left(\frac{4\pi n_0}{\lambda_0}\right)^2 \sin^2\left(\frac{\theta}{2}\right) \qquad (3)$$

where R_θ is the excess Rayleigh ratio at the scattering angle θ, and $K = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/(\lambda_0^4 N_A)$ is the optical constant, with c, n_0, λ_0, and N_A being the polymer concentration, solvent refractive index, the wavelength of the incident beam, and Avogadro's number, respectively.

Results and Discussions

Variable Temperature CD and ORD Measurements. First, to investigate a local conformation of polyketone **1**, we compared the variable-temperature CD of **1** with that of (S)-3-methyl-2,5-hexanedione (**3**), a model compound of polyketone **1**. Figure 1 shows the CD spectra of (a) polyketone **1** and (b) diketone **3**. Negative Cotton bands around 280 nm in CD spectra correspond to the n−π* transition of carbonyl groups. Wavelength of extremum for polyketone **1** (279 nm) is essentially the same as that of diketone **3** (280 nm). The absolute value of Δε of the Cotton effect for **1** (1.52 at 23 °C) was comparable to that for **3** (0.92 at 23 °C). Also the temperature dependence ($\partial(\Delta\epsilon)/\partial T$) of **1** was also comparable to that of **3**. Figure 2 shows the variable-temperature ORD spectra of polyketone **1** and diketone **3**. Similar to CD spectra, the intensities of molar rotation [Φ] and temperature dependencies of **1** and **3** were substantially the same. Therefore, we assume that the CD and ORD induction observed with polyketone **1** is not due to the secondary structure but to the chiral environment derived from the asymmetric carbon attached to carbonyl group.

When a polymer forms a stable helical conformation, CD intensity or optical rotation of this polymer is often much stronger than that for its low molecular weight model compound because of the additional contributions by secondary structure of the polymer.[13,14] For example, Pino and co-workers revealed poly(R)-3,7-dimethyl-1-octene forms a helical conformation in solution. In this case, the Δε of the copolymer of styrene and large excess of (R)-3,7-dimethyl-1-octene was much larger compared to that of a model compound.[13a] In contrast, experimental evidence for a stable helical conformation was not obtained through CD and ORD measurements for polyketone **1**, in this study.

Sen reported that the molar optical rotation of polyketone **1** showed only a slight temperature dependence.[6a] Consiglio reported that the molar ellipticity per chiral unit −(R)−$CH_2CHMeCO$− were substantially constant in the propene/ethene/CO terpolymer that consists of random arrangements of two units, −(R)−CH_2CHMe-CO− and −CH_2CH_2CO−, when the ratio of the two units was varied.[10] In these reports, it is also suggested that the secondary structure hardly contributes to the chirality of **1**.

Static Light-Scattering Measurement. For the analysis on the global shape of **1** in solution, the static light scattering measurement was carried out for a

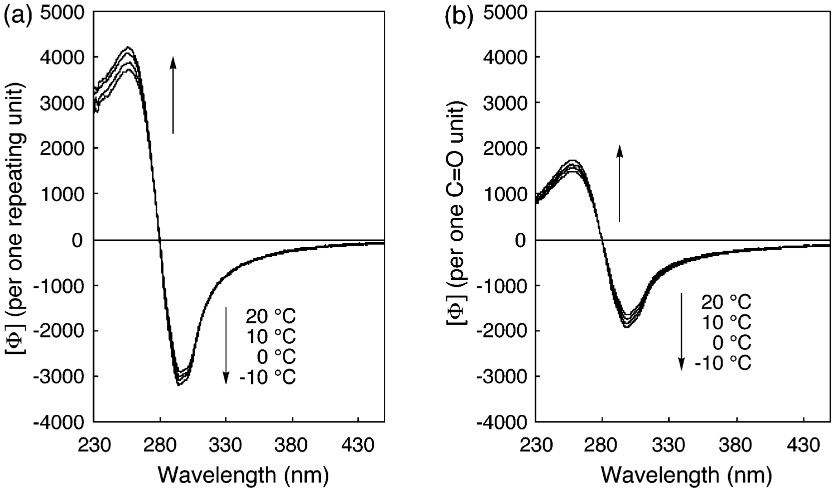

Figure 2. Variable-temperature ORD spectra of (a) polyketone **1** (0.07 mol repeating unit/L) and (b) diketone **3** (0.07 mol of ketones/L) in chloroform.

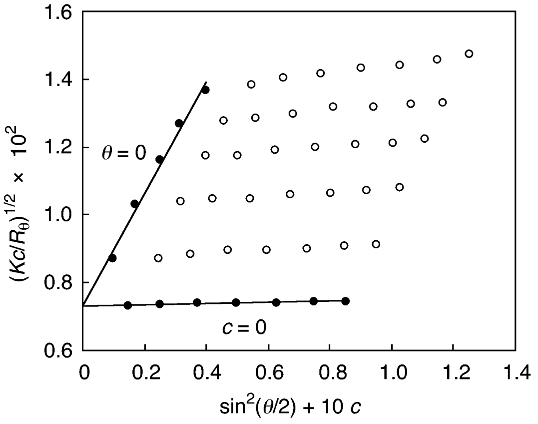

Figure 3. Berry plot for polyketone **1** in chloroform at 25 °C.

chloroform solution of polyketone **1** (M_n = 19 300, M_w = 27 600, M_w/M_n = 1.43, evaluated by GPC with a polystyrene standard) at 25 °C. Figure 3 shows the result of the Berry plot. The estimated values of M_w, A_2, and $R_{g,z}$ are 18 800, 1.21 × 10^{-4} cm^3 mol g^{-2}, and 13.6 nm, respectively. The M_w value of 18 800 estimated from light scattering is smaller than that from GPC, 27 600. This indicates an extended conformation since the GPC is compared to polystyrene standards and an extended or stiff conformation will therefore be overestimated in its molecular weight. Assuming that molecular weight distribution (M_w/M_n) for this polymer is 1.43, the value derived from GPC, M_n is calculated to be 13 100. Furthermore, to obtain number-average root-mean-square radius of gyration $R_{g,n}$, M_z was estimated to be 24 500 from Schultz−Zimm distribution. Consequently we obtained an $R_{g,n}$ value of 9.94 nm.

Consideration of Conformational Models. To evaluate the experimental value of $R_{g,n}$, we propose four conformational models of the polyketone in solution and compare the models with the experimental result.

(1) Planar Zigzag Chain Model. First, we considered a perfectly planar zigzag chain model (Figure 4a). It is known that the alternating copolymer of ethylene and carbon monoxide has a planar zigzag conformation in crystalline states.[15,16] Therefore, in this model, the length of monomeric unit was regarded as 0.380 nm, which was referred to the structure of poly(ethene-*alt*-CO).[15] Since molecular weight of monomeric unit (M) is 70.1, the number of monomeric unit was calculated to be $n = M_n/M$ = 13 100/70.1 = 187. Thus, total chain length (L) was given to be L = 187 × 0.380 = 71.1 nm, and $R_{g,n}$ was estimated to be $L/(12)^{1/2}$ = 20.5 nm. This value is much larger than the experimental one, 9.94 nm.

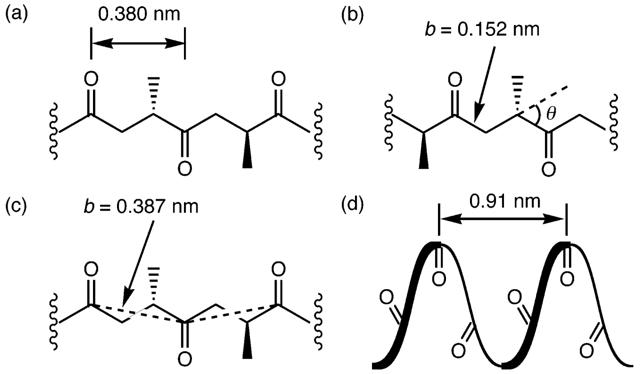

Figure 4. Four kinds of conformational models: (a) planar zigzag chain model; (b) freely rotating chain model; (c) extended freely rotating chain model; (d) 3/1 helical conformation model. The length of the monomeric unit for the zigzag model was referred to that of the crystalline structure of poly(ethene-*alt*-CO).[15]

(2) Freely Rotating Chain Model. Next, a freely rotating chain model was examined. Number-average root-mean-square end-to-end distance $\langle R^2\rangle_n^{1/2}$ and $R_{g,n}$ are given by

$$\langle R^2\rangle_n^{1/2} = \left(nb^2\,\frac{1+\cos\theta}{1-\cos\theta}\right)^{1/2} \qquad (4)$$

$$R_{g,n} = \langle R^2\rangle_n^{1/2}/6^{1/2} \qquad (5)$$

where n, b, and θ are the number of bonds, bond length, and the supplement of the bond angle, respectively.

We calculated $\langle R^2\rangle_n^{1/2}$ and $R_{g,n}$ using the following values and hypothesis (Figure 4b). The number of bonds were $n = 3 \times 187$, and bond length was b = 0.152 nm (the average of the three bonds between a carbonyl carbon and the neighboring one). For a simplicity, θ was regarded as the supplement of the regular tetrahedral angle, $\cos\theta = {}^1/_3$, although polyketone **1** contains sp^2 carbon in the main chain. The values of $\langle R^2\rangle_n^{1/2}$ and $R_{g,n}$ were obtained as 5.09 and 2.08 nm, respectively. This $R_{g,n}$ value is much smaller than the experimental result (9.94 nm).

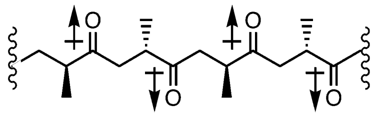

Figure 5. Cancellation of dipole moments of the adjacent carbonyl groups of polyketone **1** in the planar zigzag or s(2/1) helical conformation.

(3) Extended Freely Rotating Chain Model. We considered a virtual bond connecting between the two adjacent carbonyl carbons in the zigzag model as a statistical segment and constructed a freely rotating chain model for the chain (Figure 4c). In this case, the number of bonds is $n = 187$, equal to the number of monomeric units. The bond length is $b = 0.387$ nm, and the supplement of the bond angle is $\theta = 22.5°$. The values of $\langle R^2 \rangle_n^{1/2}$ and $R_{g,n}$ were given as 26.6 and 10.9 nm, respectively.

(4) 3/1 Helical Conformation Model. One helical conformation model was considered (Figure 4d). Chvalun and co-workers reported that an elastic film of the propene−CO copolymer with random regio- and stereoregularity crystallizes with the 3/1 helical chain conformation by an X-ray investigation at 650% elongation, the fiber repeat being 0.91 nm.[17] Thus, the total chain length (L) was given to be $L = 0.91 \times 187/3 = 56.7$ nm, and $R_{g,n}$ was estimated to be $L/(12)^{1/2} = 16.4$ nm.

Molecular Conformation of Polyketone in Solution. As stated above, the $R_{g,n}$ value of polyketone **1** is comparable to that calculated in the third model for the freely rotating chain model, in which is taken into account the factor on rigidity, or in the fourth model for the 3/1 helical conformation model. Polyketone has a larger R_g value compared to that calculated from conventional freely rotating chain model, for typical random coil chain. Also, the value of M_w derived from GPC exceeded that from static light scattering. It means that the excluded volume is estimated larger in GPC measurement. The result of large R_g is consistent with the discrepancy between the molecular weight measured by static light scattering and GPC.

We consider that the rigidity of **1** is derived from its helical conformation or its planar zigzag conformation. For example, in an s(2/1) helical conformation,[7,8] the dipole moments of the adjacent carbonyl groups are canceled with each other. Consequently, the overall dipole moment in the whole polymer chain becomes minimal (Figure 5).

Conclusion

Conformation of optically active α-methyl-γ-polyketone **1** in solution was investigated by variable-temperature CD and ORD and by static light-scattering measurements. The fact that intensity and temperature dependencies of CD and ORD for polyketone **1** are comparable those for with model diketone **3** indicates that CD and ORD induction of polyketone is not derived from the secondary structure. Meanwhile, M_w value measured by static light scattering was smaller than that measured by GPC as a polystyrene standard, suggesting an extended conformation. Examination of conformational models indicated that polyketone **1** has a relatively large R_g value, which is due to an extended or stiff structure.

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References and Notes

(1) (a) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708. (b) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143.

(2) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3138.

(3) (a) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349. (b) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013.

(4) (a) Pino, P.; Lorenzi, G. P. *J. Am. Chem. Soc.* **1960**, *82*, 4745. (b) Luisi, P. L. *Polymer* **1972**, *13*, 232.

(5) (a) Nozaki, K.; Sato, N.; Takaya, H. *J. Am. Chem. Soc.* **1995**, *117*, 9911. (b) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779.

(6) Other examples of optically active γ-polyketones: (a) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455. (b) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (c) Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suter, U. W. *Macromolecules* **1994**, *27*, 4436. (d) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

(7) Brückner, S.; De Rosa, C.; Corradini, P.; Porzio, W.; Musco, A. *Macromolecules* **1996**, *29*, 1535.

(8) De Rosa, C. *Macromolecules* **1997**, *30*, 5494.

(9) Muellers, B. T.; Park, J.-W.; Brookhart, M. S.; Green, M. M. *Macromolecules* **2001**, *34*, 572.

(10) Sesto, B.; Bronco, S.; Gindro, E. L.; Consiglio, G. *Macromol. Chem. Phys.* **2001**, *202*, 2059.

(11) Nozaki, K.; Kosaka, N.; Muguruma, S.; Hiyama, T. *Macromolecules* **2000**, *33*, 5340.

(12) (a) Cram, D. J.; Elhafez, F. A. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828. (b) Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, *30*, 2199. (c) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145. (d) *Asymmetric Organic Reactions*; Morrison, J. D.; Mosher, H. S., Eds.; Prentice Hall Inc.: Upper Saddle River, NJ, 1969. (e) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1983; Vol 2.

(13) (a) Pino, P.; Carlini, C.; Chiellini, E.; Ciardelli, F.; Salvadori, P. *J. Am. Chem. Soc.* **1968**, *90*, 5025. (b) Habaue, S.; Ajiro, H.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4088.

(14) (a) Pino, P.; Ciardelli, F.; Lorenzi, G. P.; Montagnoli, G. *Makromol. Chem.* **1963**, *61*, 207. (b) Abe, A.; Goodman, M. *J. Polym. Sci., Part A: Polym. Chem.* **1963**, *1*, 2193. (c) Porri, L.; Rossi, R.; Ingrosso, G. *Tetrahedron Lett.* **1971**, 1083. (d) van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. W.; Drenth, W.; Hezemans, A. M. F. *Macromolecules* **1983**, *16*, 1679. (e) Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 8850.

(15) Klop, E. A.; Lommerts, B. J.; Veurink, J.; Aerts, J.; van Puijenbroek, R. R. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 315.

(16) (a) Lommerts, B. J.; Klop, E. A.; Aerts, J. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 1319. (b) Aerts, J. *Polym. Bull. (Berlin)* **1996**, *36*, 645. (c) Chatani, Y.; Takizawa, T.; Murahashi, S.; Sakata, Y.; Nishimura, Y. *J. Polym. Sci.* **1961**, *55*, 811.

(17) Godovsky, Y. K.; Konyukhova, E. V.; Chvalun, S. N.; Neverov, V. M.; Abu-Surrah, A. S.; Rieger, B. *Macromol. Chem. Phys.* **1999**, *200*, 2636.

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