Macromolecules **2000,** *33,* 7093−7100

Crystalline−Noncrystalline Structure and Chain Diffusion Associated with the 180° Flip Motion for Polyethylene Single Crystals As Revealed by Solid-State ^{13}C NMR Analyses

Kazuhiro Kuwabara, Hironori Kaji, Masaki Tsuji, and Fumitaka Horii*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received May 10, 2000

ABSTRACT: The structure of the noncrystalline overlayer and molecular motion in the crystalline region for polyethylene single crystals have been investigated by solid-state ^{13}C NMR spectroscopy and transmission electron microscopy. Our previous finding that the noncrystalline overlayer is mainly composed of loose loops is confirmed for the single crystals with a typical lozenge shape by the line shape analysis of the fully relaxed DD/MAS ^{13}C NMR spectrum with the aids of ^{13}C spin−lattice and spin−spin relaxation time measurements. The occurrence of the 180° flip motion in the crystalline region is clarified by using similar methods performed in the previous work. Moreover, the chain diffusion associated with the flip motion in the crystalline region is also observed at 78 °C in the 2D ^{13}C exchange NMR spectrum. A one-dimensional random walk simulation is carried out to clarify the correlation between the 180° flip motion and the chain diffusion. The loose loop structure of the noncrystalline overlayer is still kept even after the annealing for 7 days at the temperature where the chain diffusion occurs. It is suggested that loose loops are probably the quasi-equilibrium structure for the noncrystalline overlayer of the polyethylene single crystals.

Introduction

The 180° flip motion around the chain axis and the chain diffusion associated with this flip motion for orthorhombic polyethylene crystals have been studied for many years,[1−9] and active research is still in progress. Especially, solid-state ^{13}C NMR spectroscopy is one of the most powerful methods to elucidate such molecular motions, and detailed analyses have been performed for bulk-crystallized polyethylenes and as-received (nascent) polyethylenes.[3−9] The results obtained there suggest that such a combined overall motion of the chains will be affected by the structure of the noncrystalline region: For example, some kind of restriction in conformation or molecular mobility will be one of the important factors influencing this motion.

As is well-known, lozenge-shaped single crystals with a thickness of about 10 nm are formed when a linear polyethylene sample is isothermally crystallized from a dilute solution.[10,11] Since the molecular chain axis is almost perpendicular to the basal plane of the single crystal, each chain should be folded repeatedly, and thus the folding overlayer is formed. Several structure models have already been proposed to depict the chain conformation in the overlayer of polyethylene single crystals: (a) regular sharp fold model,[12] (b) loose loop model,[13] and (c) switchboard model.[14] The detailed high-resolution solid-state ^{13}C NMR analysis revealed that the loose loop model is the most plausible model to describe the folding overlayer of the single crystal.[15] Therefore, the polyethylene single crystal is one of the most interesting samples to examine the effects of the structure in the noncrystalline region on the chain diffusion associated with the 180° flip motion.

Another important problem of the chain diffusion in the single crystal is closely associated with the interpretation of the cause why the loose loop structure is produced in the isothermal crystallization process in a dilute solution. In the case of *n*-paraffins, the two-step crystallization from the melt was revealed by time-resolved high-energy small-angle X-ray scattering:[16] At the initial stage, noninteger chain-folded crystals are preferentially formed, and then both of extended chain crystals and regularly chain-folded crystals are produced with the lapse of time as a result of the rearrangement of the chains due to the chain movement along the chain axis in the noninteger chain-folded crystals. According to this finding, the conventional crystallization process of the polyethylene single crystal may correspond to the initial stage where the noninteger chain-folded crystals are formed in paraffins. It may be, therefore, very interesting to examine the change in chain-folded structure possibly induced by the chain diffusion when the sample is annealed at the crystallization temperature.

In this paper, the crystalline−noncrystalline structure is first characterized for polyethylene single crystals to confirm the loose loop model by mainly using solid-state ^{13}C NMR spectroscopy and transmission electron microscopy (TEM). This characterization is indispensable because the lozenge-shaped single crystals were not confirmed by TEM for the sample previously used.[15] Second, the 180° flip motion and the chain diffusion are investigated in detail for this sample by the same 1D and 2D solid-state ^{13}C NMR spectroscopy as used in our previous work.[9] A theoretical calculation to estimate the extent of the segment exchange between the crystalline and noncrystalline regions through the chain diffusion is also carried out by using a somewhat different model from that used in our previous work.[9] Finally, annealing effects possibly induced on the chain-folded structure are examined also by considering the additional annealing effects on the structure defects which are more frequently included in the single crystals compared to the crystals prepared from the melt.[17]

Experimental Section

Sample. For the preparation of polyethylene single crystals,[18] NIST SRM 1489 with $M_w = 3.21 \times 10^4$ and $M_w/M_n = 1.11$ was used. The polyethylene was dissolved at 120 °C in

10.1021/ma000810v CCC: $19.00

p-xylene at a concentration of 0.05 wt %. The solution was kept at 80 °C for 20 min for primary crystallization and then heated to 96 °C with a rate of 5 °C/h for self-seeding. Next, the solution was kept at 78 °C for 24 h and then air-cooled to room temperature. These procedures were all carried out under a high-purity argon atmosphere.

Transmission Electron Microscopy. Polyethylene single crystals were picked up onto a copper grid on which a carbon supported film had been deposited and were dried under a reduced pressure. For morphological observation, specimens were shadowed with vapor-deposited gold. For observing electron diffraction patterns, specimens were decorated with vapor-deposited polyethylene but not shadowed.[19] Transmission electron microscopy was carried out with a JEOL JEM-200CS operated at 200 kV.

Solid-State ^{13}C NMR Spectroscopy. To perform solid-state ^{13}C NMR measurements, deposited polyethylene single crystals were separated from the solution by filtration, washed with acetone, and finally dried at 50 °C under a reduced pressure. One-dimensional solid-state ^{13}C NMR measurements were carried out on a JEOL JNM-GSX 200 spectrometer operating at a field strength of 4.7 T. Powderlike polyethylene crystals were packed into a magic angle spinning (MAS) zirconia rotor with a 7 mm diameter. The MAS rate was set to 3 kHz. ^{1}H and ^{13}C radio-frequency fields $\gamma B_1/2\pi$ were 62.5 and 55.6−62.5 kHz, respectively. The contact time for the cross-polarization (CP) process was 1.0 ms throughout this work. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the CH_3 line at 17.36 ppm of hexamethylbenzene crystals as an external reference. The ^{13}C chemical shift anisotropy (CSA) spectra for the crystalline components were obtained by the CPT1 pulse sequence[20] without MAS. Temperature calibration was done by the ethylene glycol method modified for solid-state measurements.[21−23]

Two-dimensional exchange ^{13}C NMR measurements were conducted on a Chemagnetics CMX-400 spectrometer under a static magnetic field of 9.4 T. The MAS rate was set to 4 kHz. The recycle delay and mixing time were 3 and 1 s, respectively. The two-dimensional exchange ^{13}C NMR spectra were taken with 64 t_1 increments of 500 μs, and the data length of FIDs was enlarged 4 times by zero filling. The number of the FID accumulation was 240. Appropriate line broadening (20 Hz) for FIDs was also employed to increase the signal/noise ratio. Other experimental conditions were almost the same as those for the JEOL JNM-GSX 200 system.

Results and Discussion

Crystalline−Noncrystalline Structure. Before analyzing the molecular motion in the crystalline region of polyethylene single crystals, we have characterized the crystalline−noncrystalline structure of this sample at room temperature. Since the proposal of the sharp fold model by Keller,[12] some models for the fold surface were proposed[12−14] and discussed from various points of views.[10,11,15,19,24−27] However, the conclusive structural model has not been established as yet. Our previous high-resolution solid-state ^{13}C NMR study revealed for the first time that the overlayer of polyethylene single crystals is composed of loose loops.[15] However, the real formation of lozenge-shaped single crystals was not examined for the same sample by transmission electron microscopy in that work. In this study, we have first taken transmission electron micrographs before starting the solid-state ^{13}C NMR measurements. As is evidently seen in Figure 1, lozenge-shaped single crystals[10,11] are confirmed to be also produced in this case. The averaged lamellar thickness is estimated to be about 12 nm, in good accord with previous results.[15]

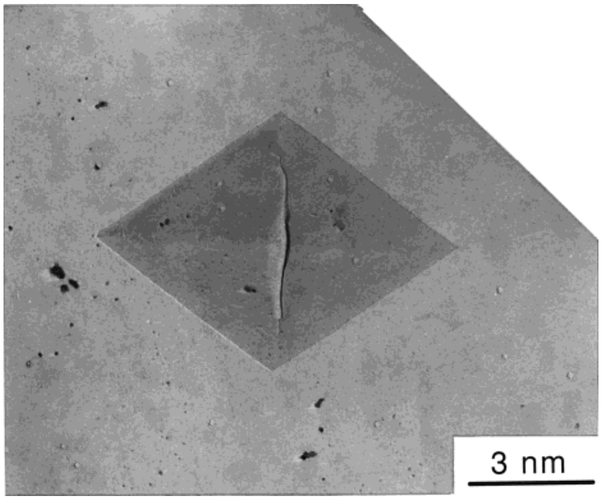

Figure 1. Transmission electron micrograph of the polyethylene single-crystal grown from a 0.05 wt % *p*-xylene solution at 78 °C by the self-seeding method.

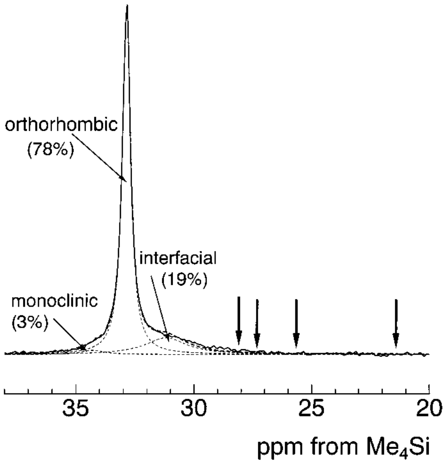

Figure 2. Fully relaxed DD/MAS ^{13}C NMR spectrum of polyethylene single crystals. Thick arrows indicate the resonance positions for the CH_2 carbons forming sharp folds of cycloalkane crystals.

A fully relaxed dipolar decoupling (DD)/MAS ^{13}C NMR spectrum of the polyethylene single crystals is shown as a solid line in Figure 2. The strong resonance line at 32.9 ppm is assigned to the crystalline component with the orthorhombic form, whereas the broad upfield tailing centered at 31 ppm is ascribed to the noncrystalline component.[15,28−30] In addition, the small downfield tailing at 34.3 ppm should be assigned to another crystalline component with the monoclinic form.[15,31,32] The result of the line shape analysis, which is shown by broken lines, will be described later.

For the purpose of obtaining more detailed information about the crystalline and noncrystalline components, ^{13}C spin−lattice relaxation times (T_{1C}) and ^{13}C spin−spin relaxation times (T_{2C}) have been measured. In Figure 3, the logarithmic peak intensities of the crystalline component, which were measured by the CPT1 pulse sequence,[20] are plotted against the decay time for the T_{1C} relaxation. Similarly to the cases of other polyethylene samples,[15,28−30] the crystalline component appearing at 32.9 ppm is found to also consist of three components with different T_{1C} values. The composite curve (thick broken line) of the three components, obtained by the least-squares method, is in good accord with the observed data. We also tried to analyze the T_{1C} relaxation process by using the one-dimensional chain diffusion equation previously reported.[5,6] However, the relaxation curve for this sample was found not

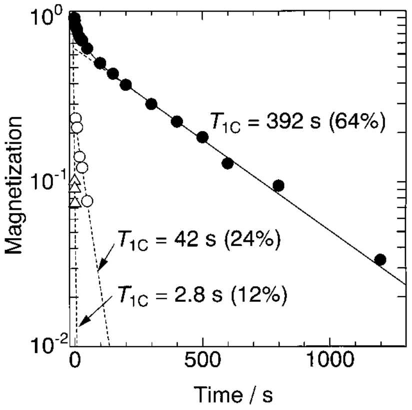

Figure 3. ^{13}C spin–lattice relaxation behavior of the crystalline component of polyethylene single crystals obtained by the CPT1 pulse sequence.

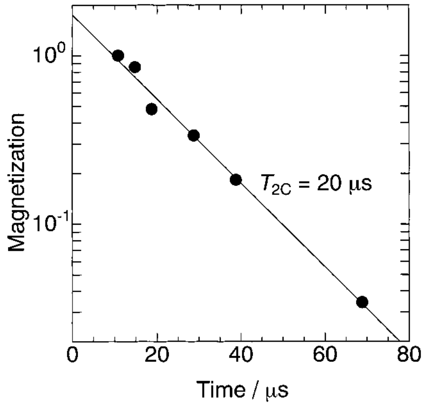

Figure 4. ^{13}C spin–spin relaxation behavior of the noncrystalline component of polyethylene single crystals obtained by the ^{13}C spin-echo pulse sequence.

to be well described by that equation. It is, therefore, concluded that three crystalline components with T_{1C} values of 392, 42, and 2.8 s exist in this sample. For convenience, these components are hereafter referred to as the rigid crystalline, less mobile crystalline, and mobile crystalline components in the order of decreasing T_{1C} values similarly to the case of metallocene-catalyzed linear low-density polyethylene.[9]

The T_{1C} relaxation process for the noncrystalline component appearing at 31 ppm has been measured by the saturation recovery pulse sequence modified for solid-state measurements[15,29,30] and well analyzed in terms of a single component with T_{1C} = 0.35 s. The noncrystalline region seems to consist of only one component judging from the T_{1C} value which is associated with the spectral density of molecular motion on the order of 10^8 Hz.

In the bulk-crystallized HDPE, the noncrystalline region is further separated into the crystalline–amorphous interfacial and rubbery amorphous regions by using the difference in T_{2C} under a condition without ^1H dipolar decoupling.[15,29,30] Figure 4 shows the ^{13}C spin–spin relaxation process of the noncrystalline component at 31 ppm shown in Figure 2, which was measured under the suppression of the crystalline component by the ^{13}C spin-echo pulse sequence without ^1H dipolar decoupling during the T_{2C} decay period.[15] This relaxation process is found to be well described in terms of a single component with T_{2C} = 20 μs. In the analogy of the previous assignment,[15] this noncrystalline component should be assigned to the crystalline–amorphous interfacial component because the order of the T_{2C} value of this component is in good accord with that of the interfacial component.

Judging from the lamellar thickness of 12 nm and the degree of crystallinity of 0.81 (see below), the thickness of the noncrystalline overlayer is estimated to be about 1.1 nm. Previous theoretical work made by using the lattice model for bulk-crystallized polyethylene revealed that the thickness of 15–20 nm is required as the crystalline–amorphous interfacial region for the noncrystalline region to produce the rubbery amorphous phase.[33] In fact, the bulk-crystallized HDPE samples have the rubbery amorphous component together with the interfacial component with a thickness of about 3 nm.[15,30] In the case of the polyethylene single crystals, the thickness of the overlayer may be too thin to produce the rubbery–amorphous component.

The spectrum of the interfacial component can be well described by a single Lorentzian curve. By similarly assuming Lorentzian curves for the resonance lines of the crystalline components with the orthorhombic and monoclinic forms, a line shape analysis has been carried out for the fully relaxed DD/MAS ^{13}C NMR spectrum for the single crystals as shown in Figure 2. It is found that the composite curve of the three components, which is indicated as a thick broken line, is in good accord with the observed curve. The mass fractions determined as integrated intensity fractions for the monoclinic crystalline, orthorhombic crystalline, and interfacial components are 0.03, 0.78, and 0.19, respectively. Since the lamellar thickness is about 12 nm as described above, the thickness of the crystalline region is about 9.4 nm. Thick arrows in Figure 2 indicate the resonance positions for the CH_2 carbons forming sharp folds in cycloalkane crystals.[34] No resonance lines appear at the positions indicated by arrows. We also measured DD/MAS ^{13}C NMR spectra at 60–100 °C by the 45° single pulse sequence. Here the pulse delay time was set to 10–30 s, since the T_{1C} values of the CH_2 carbons in the folds for cycloalkane crystals are of the order of 30 s in this temperature range and the values for sharp folds for polyethylene will be assumed to be shorter than the former T_{1C}'s.[34] No resonance line assignable to the folding CH_2 carbons were also detected at higher temperatures. These facts indicate that the fraction of the CH_2 carbons forming sharp folds may be estimated to be less than 0.05 against the total CH_2 carbons in the overlayer of the polyethylene single crystals under the present NMR sensitivity and resolution.

The molecular chain conformation in the overlayer is considerably restricted, as revealed by the short T_{2C} value of the interfacial component. However, T_{1C} is almost equivalent to that of the rubbery–amorphous component.[15,29,30] It is, therefore, concluded that the chain conformation in the overlayers is not as restricted as suggested by the regularly folded reentry of the molecular chain in the adjacent crystalline sequence of the same (110) plane.[25] In other words, it is also confirmed that the noncrystalline overlayer is composed of loose loops.[13,15] These loose loops may be composed of about 20 CH_2 units as average judging from the thickness (1.1 nm) of the overlayer.

Molecular Motion in the Crystalline Region. Figure 5 shows CP/MAS ^{13}C NMR spectra of the single crystals measured at different temperatures. The half-width is found to remarkably broaden above 60 °C, indicating the occurrence of the molecular motion with

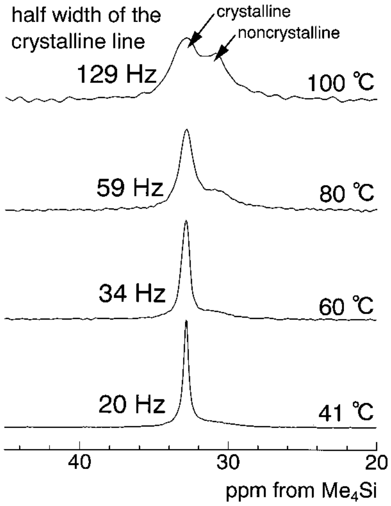

Figure 5. CP/MAS ^{13}C NMR spectra of polyethylene single crystals at different temperatures.

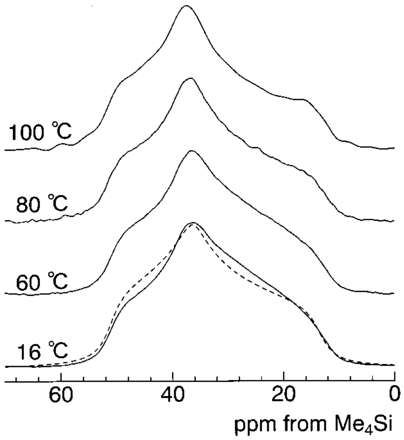

Figure 6. ^{13}C CSA spectra of the crystalline component of polyethylene single crystals: solid line, observed; broken line, simulated for the orthorhombic crystals in the rigid state.

the rate corresponding to the ^{1}H dipolar decoupling field (about 10^5 Hz).[7,9,35−38] As shown in our previous work,[9] similar broadening of the crystalline resonance line was also observed above about 60 °C for the metallocene-catalyzed linear low-density polyethylene sample that was isothermally crystallized at 110 °C from the melt. The ^{13}C CSA analysis previously made for this sample revealed that such broadening is due to the occurrence of the 180° flip motion with the order of about 10^5 Hz around the chain axis.

To confirm the occurrence of the same type of 180° flip motion for the single crystals, ^{13}C CSA spectra have been selectively measured at different temperatures for the crystalline component of this sample by the CPT1 pulse sequence[20] with the T_{1C} decay of 2.0 s. In these spectra, the interfacial component completely disappears due to the short T_{1C} values. Figure 6 shows the ^{13}C CSA spectra of the crystalline component thus obtained at different temperatures for the polyethylene single crystals. The broken line denotes the CSA spectrum simulated for the orthorhombic form of polyethylene in the rigid state. Though the molecular motion with the rate of about 10^5 Hz occurs above 60 °C, the ^{13}C CSA line shape at each temperature is not significantly different from the line shape in the rigid state.

The assignment for the principal axes of the chemical shift tensor for the CH_2 carbon of polyethylene was made in the rigid orthorhombic crystals.[39−42] The σ_{11} axis is assigned to the direction parallel to the H−H vector, the σ_{22} axis to the direction parallel to the H−C−H angle bisector, and the σ_{33} axis to the direction parallel to the molecular chain axis. According to this assignment, the CSA spectrum will give the same line shape as in the rigid state when the respective crystalline chains undergo the 180° flip motion around the molecular chain axis.[39−42] It is, therefore, concluded that the 180° flip motion around the molecular chain axis[1,7−9] also occurs above about 60 °C with a rate of about 10^5 Hz in the crystalline region for the polyethylene single crystals. More direct evidence of the 180° flip motion was obtained by the analysis of the ^{13}C−^{13}C dipolar coupling for the crystalline component in ultradrawn polyethylene fibers in the similar temperature region.[8] In addition, we also pointed out that the 180° flip motion is allowed to occur in other ultradrawn polyethylene fibers, because similar line broadening is observed for the CP/MAS ^{13}C NMR spectrum above about 80 °C.[32]

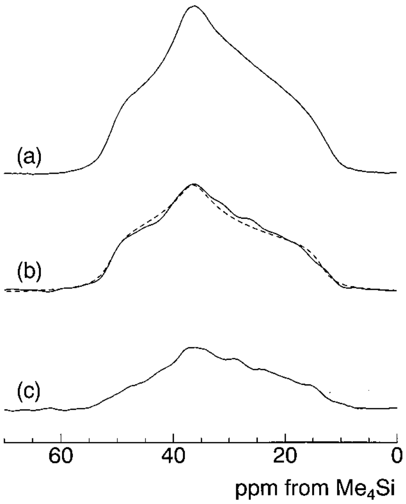

Figure 7. Separation of ^{13}C CSA spectrum of the crystalline component (a) into the spectrum of the rigid crystalline component (b) and the composite spectrum of the less mobile crystalline and mobile crystalline components (c) for polyethylene single crystals. (a) and (b) were obtained by the CPT1 pulse sequence. (c) is the difference spectrum (a) − (b). The broken line indicates the simulated spectrum for the rigid orthorhombic crystals.

There are slight deviations from the rigid line shape in the CSA spectra at 16−100 °C. These deviations may be due to the twisting motion along the *c*-axis[43] or some conformational defects.[44] As shown in our previous work,[9] similar disordered ^{13}C CSA spectra were observed above about 60 °C for the crystalline component of the linear low-density polyethylene sample crystallized from the melt. In that sample, however, the line shape at 16 °C was in good accord with that in the rigid state. These results indicate that the polyethylene single crystals contain more defects in the crystalline region[17] and thus undergo more enhanced motion compared to the linear low-density polyethylene sample crystallized from the melt. In this case we simply compare these samples that were obtained by cooling to room temperature after the crystallization at 110 °C from the melt or at 78 °C in solution without any annealing above 50 °C even during the drying process.

By using the difference in T_{1C}, the CSA spectrum at 16 °C has been resolved into two components: the rigid and other crystalline components. Figure 7 shows the

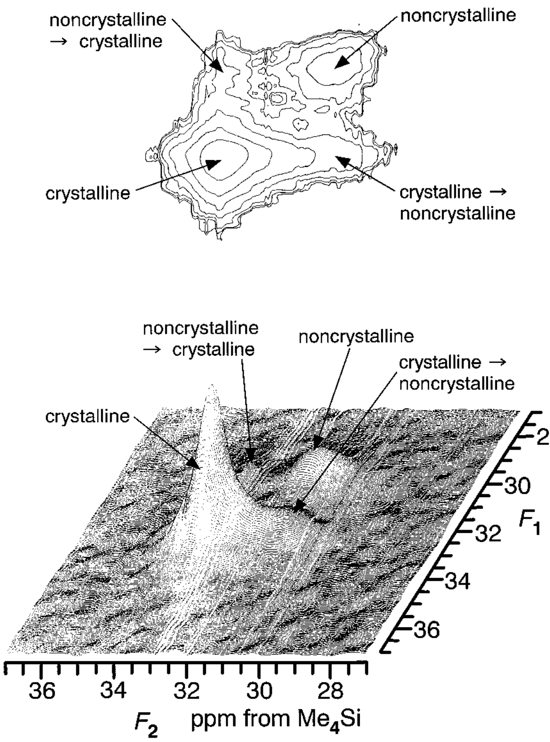

Figure 8. DD/MAS 2D exchange ^{13}C spectrum of polyethylene single crystals measured at 78 °C, with $t_m = 1$ s and a recycle delay of 3 s.

CSA spectra thus obtained for the rigid crystalline component (b) and the less mobile crystalline and mobile crystalline components (c) together with the total crystalline component (a). Here, spectrum (b) has selectively been measured by the CPT1 pulse sequence[12] by setting the T_{1C} decay time to 210 s. In spectrum (b), the less mobile crystalline and mobile crystalline components almost disappear due to their shorter T_{1C} values. Spectrum (c) is obtained by the subtraction of spectrum (b) from spectrum (a). Interestingly, spectrum (b) is in good accord with the line shape in the rigid sate which is indicated by a broken line. In contrast, spectrum (c) seems to significantly deviate from the line shape in the rigid state. These results imply that some crystalline region will be well ordered in the rigid state at 16 °C for the single crystals as for the linear low-density polyethylene sample crystallized from the melt, whereas other crystalline regions contributing the less mobile and mobile crystalline components may contain conformational defects.[43,44]

(c) Chain Diffusion along the Molecular Chain Axis in the Crystalline Region. As shown in our previous work,[9] the multistep forward and backward 180° flip motions around the molecular chain axis induce the chain diffusion along the chain axis in the crystalline region for the linear low-density polyethylene sample crystallized from the melt. Although that sample contains butyl branches with a concentration of about one branch per 100 CH_2 units, about 1% of the 180° flip motions contribute to the chain diffusion. It is an open question whether such chain diffusion is also observed in the polyethylene single crystals, because the noncrystalline overlayer composed of loose loops in this sample is considerably restricted in molecular mobility.

Figure 8 shows a DD/MAS 2D exchange ^{13}C NMR spectrum of the polyethylene single crystals, which was measured at 78 °C with a mixing time of 3 s and a recycle delay of 5 s without using the CP technique. Two cross-peaks are clearly observed together with two larger diagonal peaks assigned to the crystalline and noncrystalline components. The existence of the cross-peaks indicates the occurrence of exchange between the crystalline and noncrystalline components through the chain diffusion described above for the single crystals, in good accord with the previous results for different types of polyethylene samples.[4,9] The total mole fraction F_T for the CH_2 units that are transferred from the noncrystalline region to the crystalline region has been estimated to be 0.45 against the total noncrystalline component. Here, this value is obtained as an average integrated fraction for five slice spectra along the F_2 axis including the cross-crystalline and diagonal noncrystalline lines. Here, the T_{1C} effect on the F_T value must be also small in this case as estimated in the previous paper.[1]

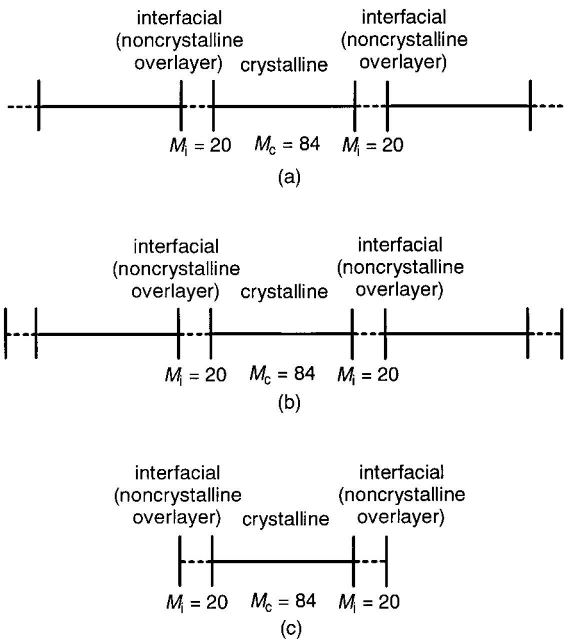

Figure 9. Schematic structural model of the one-dimensional random walk for the chain diffusion in polyethylene single crystals. The characters "M_c" and "M_i" denote the numbers of methylene units in the crystalline and interfacial stems, respectively: (a) No restriction in the range for the chain diffusion. (b) The movement is restricted in the range within $\pm(2M_i + M_c)$, where positive and negative numbers correspond to the movements to the right and left directions, respectively. (c) The movement is restricted in the range within $\pm M_i$.

To evaluate the level of the F_T value of 0.45, a simple simulation has been made by using a one-dimensional random walk model for the chain diffusion due to the multistep forward and backward 180° flip motions. In this simulation, the following assumptions are made: (1) As shown in Figure 9, the crystalline and interfacial (noncrystalline overlayer) stems consist of 84 and 20 CH_2 units, respectively. (2) The 180° flip motions induce forward and backward CH_2 movements, which correspond to steps along the chain axis in the crystalline region. (3) The probabilities for the respective forward and backward movements are 0.50 for each step, which is really described in terms of the one-dimensional random walk model. (4) The stem lengths for the crystalline and interfacial regions stay constant during the chain diffusion. (5) The real 180° flip motion may be independently induced in each crystalline stem. In other words, the net movement of the crystalline stem

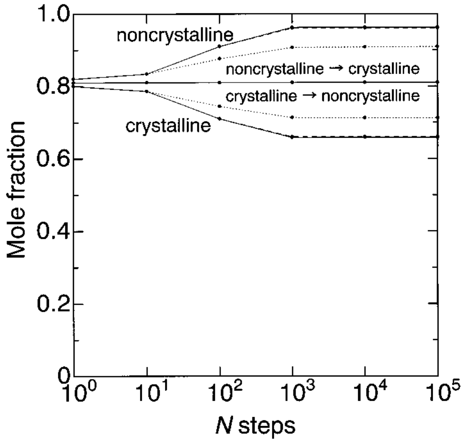

Figure 10. Mole fraction (F_T) versus number N of steps for each component for polyethylene single crystals. Solid, broken, and dotted lines correspond to cases (a), (b), and (c) in Figure 9, respectively.

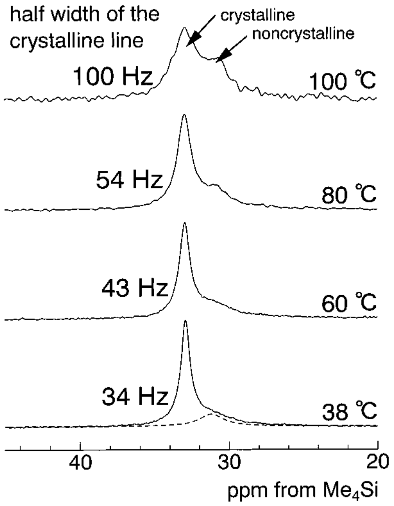

Figure 11. CP/MAS ^{13}C NMR spectra measured at different temperatures for polyethylene single crystals annealed at 100 °C for 7 days.

may be limited within a certain area from the surface of the crystallite. Therefore, we also assume restrictions for the ranges allowed for the chain diffusion as shown in Figure 9b,c. Other conditions for this simulation are the same as described in our previous work.[9]

Figure 10 shows the results of the random walk simulation for the chain diffusion under the three cases (a)−(c) described in Figure 9. It should be noted that there is almost no difference in simulation results between case (a) and case (b), indicating that the chain diffusion may be restricted around the regions associated with the first neighboring crystalline stems. At $N = 10^5$, which corresponds to the 180° flip rate of 10^5 Hz, F_T can be determined as 0.52−0.80 in the three cases. This simulated value is somewhat larger than the experimentally obtained value of 0.45. To fulfill the F_T value of 0.45, N should be about 10^2 because F_T is 0.35−0.50 for $N = 10^2$ as shown in Figure 10. Similarly to the results for the linear low-density polyethylene sample crystallized from the melt,[9] this fact also indicates that all 180° flip motions do not contribute to the chain diffusion in the crystalline region. There may be some restriction due to the structure of the noncrystalline overlayer for the polyethylene single crystals.

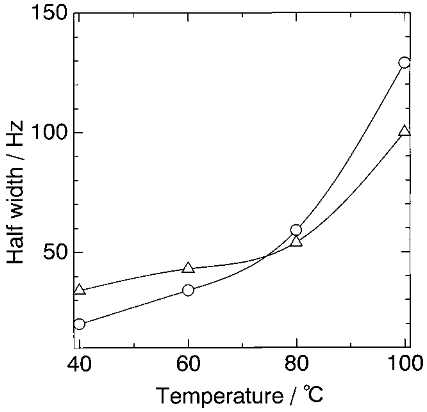

Figure 12. Temperature dependence of the line width of the crystalline component of polyethylene single crystals: ○, unannealed; △, annealed at 100 °C for 7 days.

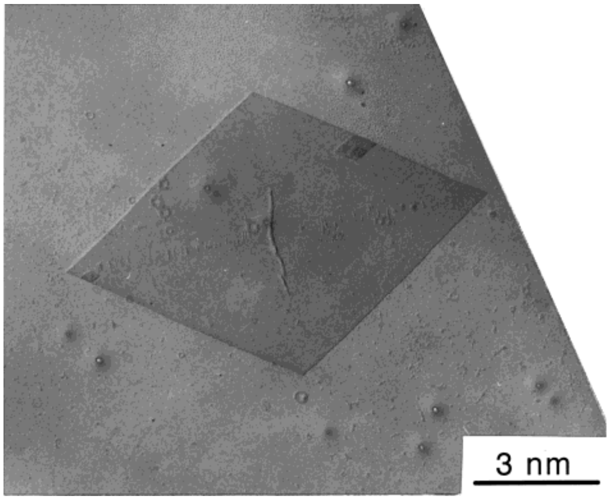

Figure 13. Transmission electron micrograph of the polyethylene single-crystal annealed at 100 °C for 7 days.

Effects of Annealing on the 180° Flip Motion and the Chain Diffusion. The chain diffusion in the crystalline region of polyethylene accompanies the molecular motion along the chain axis in the noncrystalline overlayer region. If the overlayer structure of the single crystals as prepared would be formed in a nonequilibrium state, long-term annealing at temperatures where the chain diffusion occurs could induce the modification to the structure in the quasi-equilibrium state. It is, therefore, of interest to examine the possibility of the structural change by such long-term annealing and to clarify which model is the most appropriate for the noncrystalline overlayer structure in the quasi-equilibrium state. To clarify the effect of the chain diffusion on the overlayer structure, we have annealed the polyethylene single crystals at 100 °C for 7 days under a N_2 atmosphere. It has been confirmed by transmission electron microscopy as described later that no lamellar thickening occurs under such annealing conditions, in good accord with the previous results.[17]

Figure 11 shows CP/MAS ^{13}C NMR spectra of the single crystals annealed at 100 °C for 7 days, which were measured at different temperatures. As shown in the broken line at 38 °C, the resonance line assigned to the interfacial component still remains even after long-term annealing at 100 °C. In other words, loose loops are considered to be the quasi-equilibrium overlayer structure for the polyethylene single crystals.

Compared to the CP/MAS ^{13}C NMR spectra of the unannealed sample shown in Figure 5, two types of

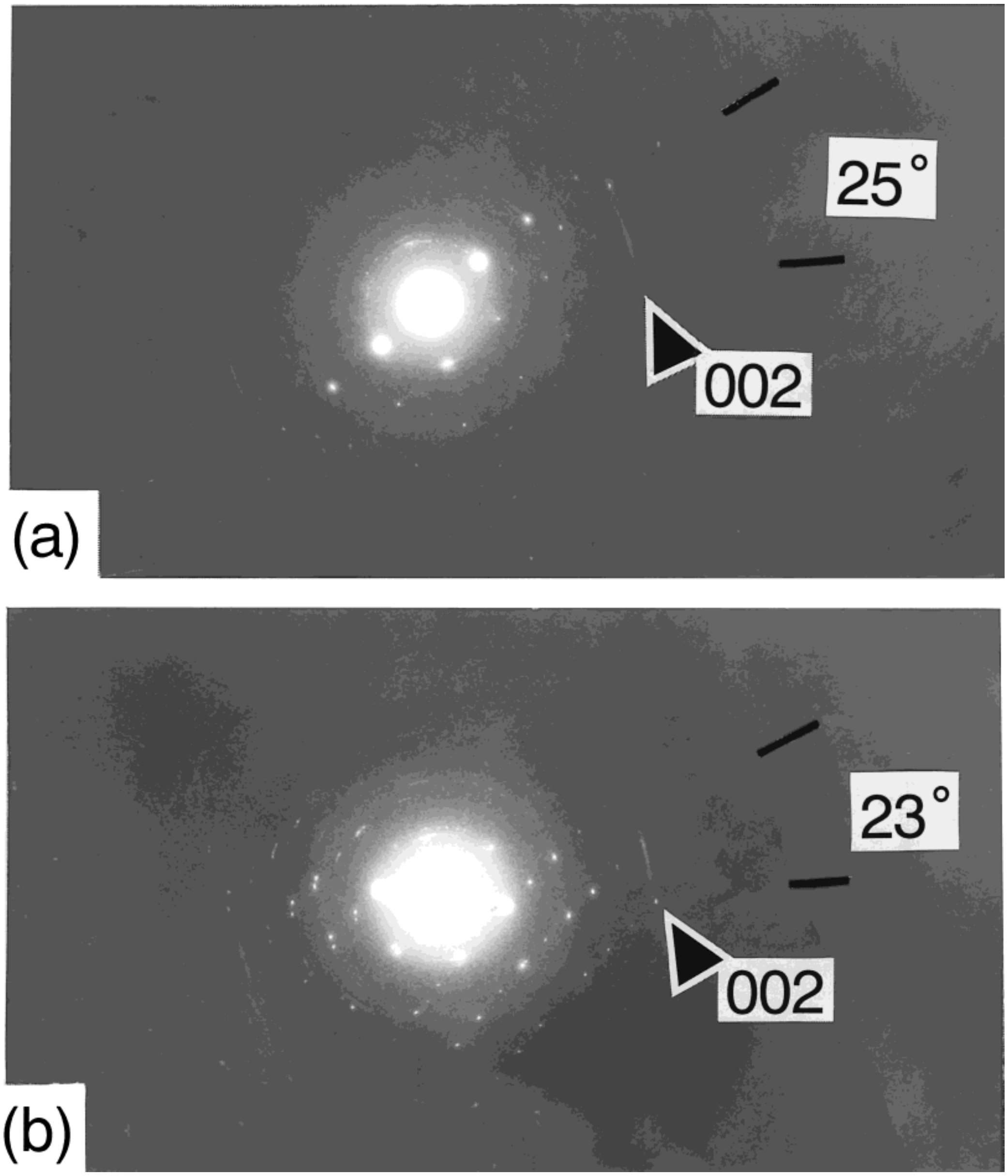

Figure 14. Electron diffraction patterns of surface-decorated polyethylene single crystals: (a) unannealed; (b) annealed at 100 °C for 7 days. In each pattern, spotlike reflections are attributed to the mother crystal (polyethylene single crystal) and arc-shaped ones to the rodlike daughter crystals vapor-deposited on the mother crystals.[19]

changes are observed in line width for the crystalline component. Figure 12 shows the temperature dependence of the line width of the crystalline resonance line for the unannealed and annealed samples. The line width for annealed sample is significantly broader at 40−60 °C compared to that for the unannealed sample. In contrast, the line width for the annealed sample is narrower than that for the unannealed sample at 80−100 °C. To compare the mobility of the crystalline component at 40 °C, the T_{1C} value has been also measured for the annealed sample. The T_{1C} value obtained for the rigid crystalline component of the annealed sample is 690 s, which is much longer than the value (390 s) for the unannealed sample.

It is known that defects in the crystalline region of polyethylene single crystals can be reduced by annealing.[17] The increase in the T_{1C} value at 40 °C confirms the reduction in such defects. From a simple point of view, the reduction in defects would cause the decrease in the crystalline line width at 40−60 °C. However, experimental results reveal the increase in the line width as shown in Figure 12. It is considered that the unannealed single crystals also involve the distribution of the local structure that should be reflected on the line width at 40−60 °C. However, this type of distribution will be partly averaged by the enhanced motion induced in the presence of the local defects, resulting in narrower line widths at 40−60 °C. In contrast, such motion may be hindered for the annealed sample due to the reduction in defects, leading to the increase in line width at 40−60 °C. The decrease in the crystalline line width at 80−100 °C for this sample by annealing also indicates the effect of the reduction in defects. Namely, the 180° flip motion that produces line broadening at 80−100 °C may be somewhat hindered by the decrease in defects after annealing.

To examine whether the shape of polyethylene single crystal changes by the annealing, we have observed the annealed polyethylene single crystals by transmission electron microscopy. Figure 13 shows a transmission electron micrograph of the polyethylene single crystal annealed at 100 °C for 7 days. No remarkable change is observed for the lozenge-shaped polyethylene single crystal even after such long-term annealing.

Since there is a possibility that the folding direction may change by the annealing, we have taken electron diffraction patterns[19] for the unannealed and annealed polyethylene single crystals, both of which were surface-decorated with vapor-deposited polyethylene. Figure 14a shows an electron diffraction pattern from the (100) sector of the "unannealed" polyethylene single crystal. The arc-shaped (002) reflection is observed and is attributed to the polyethylene rodlike crystals overgrown on the fold surface of the unannealed mother single crystal. The azimuthal angle of the (002) reflection is 25°, and this angle directly shows the angular distribution of the *c**-axis of the vapor-deposited rodlike crystals of polyethylene. In Figure 14b, an electron diffraction pattern is shown which was obtained from the (100) sector of the "annealed" polyethylene single crystal. The azimuthal angle of the (002) reflection, in this case, is 23°. This value is almost the same as the one for the unannealed sample. These results indicate that the folding direction is conserved even after the long-term annealing.

Conclusions

The structure of the noncrystalline overlayer and the molecular motions in the crystalline region of polyethylene single crystals have been investigated by solid-state ^{13}C NMR spectroscopy and transmission electron microscopy. In this study, we have obtained following conclusions.

(1) The fully relaxed DD/MAS ^{13}C NMR spectrum has revealed that the polyethylene single crystals include a noncrystalline component with a mole fraction of 0.19. However, almost no resonance line assigned to sharp folds has been observed. T_{2C} analyses have revealed that mobility of the noncrystalline component is considerably constrained compared to the rubbery amorphous component reported for bulk-crystallized polyethylene. It is, therefore, confirmed that the noncrystalline overlayer of polyethylene single crystals is mainly composed of loose loops with the average length of about 20 CH_2 units, in good accord with our previous result.

(2) Marked broadening of the resonance line for the crystalline component has been observed at 60−100 °C with increasing temperature in CP/MAS ^{13}C NMR spectra. This result reveals that the spectral density of motions near 10^5 Hz is not negligible over this temperature range. In contrast, no change is observed for ^{13}C CSA spectra in this temperature range. These results indicate, in accord with the previous results for different polyethylene samples, that the 180° flip motion around the chain axis with about 10^5 Hz also occurs in the crystalline region for the polyethylene single crystals.

(3) Despite the constrained structure of the noncrystalline overlayer of the single crystals compared to the rubbery amorphous region of polyethylene, the two-dimensional ^{13}C exchange NMR spectrum measured at 78 °C clearly shows the segmental exchange between the crystalline and noncrystalline regions as a result of the chain diffusion.

(4) Even in the presence of the chain diffusion, no remarkable change has been observed in the structure of the noncrystalline overlayer by annealing at 100 °C for 7 days. Therefore, the loose loops seem to be the quasi-equilibrium structure for the noncrystalline overlayer of polyethylene single crystals.

References and Notes

(1) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymer Solids*; Wiley: New York, 1967.
(2) Ward, I. M.; Hadly, D. W. *An Introduction to the Mechanical Properties of Solid Polymers*; Wiley: New York, 1995.
(3) VanderHart, D. L. *J. Magn. Reson*. **1987**, *72*, 13.
(4) Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 5288.
(5) Robertson, M. B.; Ward, I. M.; Klein, K. G.; Packer, K. J. *Macromolecules* **1997**, *30*, 6893.
(6) Klein, P. G.; Robertson, M. B.; Driver, M. A. N.; Ward, I. M.; Packer, K. J. *Polym. Int.* **1998**, *47*, 76.
(7) Hillebrand, L.; Schmidt, A.; Bolz, A.; Hess, M.; Veeman, W.; Meier, R. J.; van der Velden, G. *Macromolecules* **1998**, *31*, 5010.
(8) Hu, W.-G.; Boeffel, C.; Schmidt-Rohr, K. *Macromolecules* **1999**, *32*, 1611; **1999**, *32*, 1714.
(9) Kuwabara, K.; Kaji, H.; Horii, F. *Macromolecules* **2000**, *33*, 4453.
(10) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.
(11) Wunderlich, B. *Macromolecular Physics*; *Crystal Structure, Morphology, Defects*; Academic: New York, 1973; Vol. 1.
(12) Keller, A. *Philos. Mag.* **1957**, *2*, 1171.
(13) Fisher, E. W.; Lorentz, R. *Kolloid Z. Z. Polym*. **1963**, *89*, 97.
(14) Flory, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 2857.
(15) Kitamaru, R.; Horii, F.; Murayama, K. *Macromolecules* **1986**, *19*, 636.
(16) Ungar, G.; Keller, A. *Polymer* **1986**, *27*, 1835.
(17) Wunderlich, B. *Macromolecular Physics*; *Crystal Nucleation, Growth, Annealing*; Academic: New York, 1976; Vol. 2, and related references therein.
(18) Blundell, D. J.; Keller, A. *Polym. Lett.* **1966**, *4*, 481.
(19) Tsuji, M.; Ihn, K. J. *Bull. Inst. Chem. Res., Kyoto Univ.* **1995**, *72*, 429.
(20) Torchia, D. A. *J. Magn. Reson*. **1978**, *30*, 613.
(21) Kaplan, K. L.; Bovey, F. A.; Cheng, M. N. *Anal. Chem.* **1975**, *47*, 1703.
(22) English, A. D. *J. Magn. Reson*. **1984**, *57*, 491.
(23) Murata, T.; Horii, F.; Fujito, T. *Proc. Soc. Solid-State NMR Polym*. **1994**, *7*, 29.
(24) Sadler, D. M.; Keller, A. *Macromolecules* **1977**, *10*, 1128.
(25) Sadler, D. M.; Keller, A. *Science* (*Washington, D.C.*) **1979**, *203*, 263.
(26) Thomas, E. L., Ed. *Materials Science and Technology*; *Structure and Properties of Polymers*; VCH Publishers Inc.: New York, 1993; Vol. 12, and related references therein.
(27) Kavassalis, T. A.; Sundararajan, P. R. *Macromolecules* **1993**, *26*, 4144.
(28) Kimura, T.; Neki, K.; Tamura, N.; Horii, F.; Nakagawa, M.; Odani, H. *Polymer* **1992**, *25*, 4114.
(29) Kitamaru, R.; Horii, F.; Zhu, Q.; Bassett, D. C.; Olley, R. H. *Polymer* **1994**, *35*, 1171.
(30) Kuwabara, K.; Kaji, H.; Horii, F.; Bassett, D. C.; Olley, R. H. *Macromolecules* **1997**, *30*, 7516.
(31) VanderHart, D. L. *Polymer* **1984**, *25*, 830.
(32) Kuwabara, K.; Horii, F. *Macromolecules* **1999**, *32*, 5600.
(33) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17*, 862.
(34) Möller, M.; Gronski, W.; Cantow, H.-J.; Höcker, H. *J. Am. Chem. Soc.* **1984**, *106*, 5093.
(35) Suwelack, D.; Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1980**, *73*, 2559.
(36) Rothwell, W. P.; Waugh, J. S. *J. Chem. Phys.* **1981**, *74*, 2721.
(37) Takegoshi, K.; Hikichi, K. *J. Chem. Phys.* **1991**, *94*, 3200.
(38) Chen, Q.; Yamada, T.; Kurosu, H.; Ando, I.; Shiono, T.; Doi, Y. *J. Mol. Struct.* **1991**, *263*, 319.
(39) VanderHart, D. L. *J. Chem. Phys.* **1976**, *64*, 830.
(40) Opella, S. J.; Waugh, J. S. *J. Chem. Phys.* **1977**, *66*, 4919.
(41) VanderHart, D. L. *Macromolecules* **1979**, *12*, 1232.
(42) Nakai, T.; Ashida, J.; Terao, T. *J. Chem. Phys.* **1988**, *88*, 6049.
(43) Boyd, R. H. *Polymer* **1985**, *26*, 1123.
(44) Reneker, D. H.; Mazur, J. *Polymer* **1988**, *29*, 3.

MA000810V