Polymer Branching

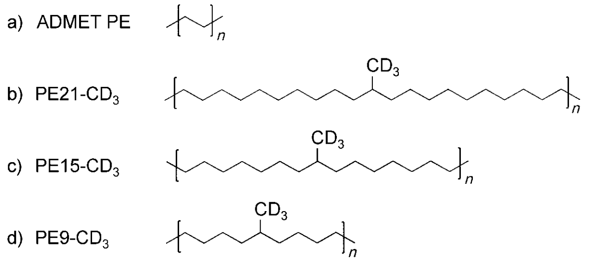
DOI: 10.1002/anie.200900377

Local and Collective Motions in Precise Polyolefins with Alkyl Branches: A Combination of ^{2}H and ^{13}C Solid-State NMR Spectroscopy[**]

Yuying Wei, Robert Graf, John C. Sworen, Chi-Yuan Cheng, Clifford R. Bowers, Kenneth B. Wagener, and Hans Wolfgang Spiess**

Molecular motions are of utmost importance for the macroscopic properties of polymers.[1] In linear polymers, such as polyethylene (PE), branching changes the mobility, and has a pronounced effect on the mechanical properties,[2] such as processablity and drawability, and has therefore been studied in detail.[3] In the systems studied previously, and in particular in commercial PE, the side chains are irregularly distributed along the main chain, which results in complexity and uncertainty of the influence of defects. Therefore, it is highly desirable to study the effect of branching on molecular motions in polyolefins with exactly defined branches, both with regard to the chemical nature of the branch and the distance between the branches along the chain. Once such samples are available, both the rate and the amplitude of chain motion can be studied in a site-selective fashion with advanced solid-state NMR spectroscopic methods.[4] Moreover, owing to the sensitivity of ^{13}C chemical shifts on conformation and torsional angles,[5] NMR can also probe structure and dynamics of the chain defects imposed by the branch. The effect of branching on mobility is particularly interesting in the crystalline regions of semicrystalline polymers provided branches can be incorporated, which suggests methyl groups as branches. By combining state-of-the-art synthetic chemistry and NMR spectroscopy, several questions can be addressed, namely: the nature of the motion of the branches, how the branches alter the geometry and mobility of adjacent chain segments, whether the motion of one branch influences the motion of neighboring branches (collective motion, rotator phase), and whether *gauche* conformers can be incorporated in the crystalline regions. Indeed, such precisely defined polyolefins have recently been prepared by acyclic diene metathesis (ADMET) polycondensation.[6] This method allows the primary structure, that is, branch identity and spacer, to be controlled. Moreover, the methyl branches can be selectively deuterated such that the mobility of the branches themselves can be conveniently studied by ^{2}H NMR.[7]

Four precise polyolefins, including three perdeuterated polymers, were prepared to study the conformational defects: PE, PE21-CD_3, PE15-CD_3, and PE9-CD_3, where the number after PE indicates the number of carbon atoms between two adjacent CD_3 branches along the backbone (Scheme 1). The model polyolefins were synthesized by ADMET step polymerization using a modification of the procedure described previously,[6] and the basic characterization is presented in Table 1 and in the Supporting Information. The morphology and packing of the systems have been studied before by X-ray scattering and electron microscopy.[8]



Scheme 1. Precisely branched polymers. a) ADMET PE, with no branching, b–d) PE$_n$-CD_3, with deuterated methyl groups on each and every *n*th carbon.

Table 1: Polymer characterization data.

Model Polymer	M_w[a] [kg mol^{-1}]	PDI[b]	T_m[c] [K]	T_c[c] [K]	ΔH_m[c] [J g^{-1}]	T_g[d] [K]
ADMET PE	15	2.6	407	386	205	N/A
PE21-CD_3	56.1	1.9	335	329	101	229
PE15-CD3	53.1	1.9	312	302	79	229
PE9-CD3	56.5	1.8	264	239	30	230

[a] From gel permeation chromatography (GPC) and using polystyrene standards. [b] Polydispersity index M_w/M_n determined from GPC. [c] From differential scanning calorimetry (DSC). [d] Glass transition temperature obtained from reference [6b].

---

[*] Y. Wei, Dr. J. C. Sworen, Dr. C.-Y. Cheng, Prof. Dr. C. R. Bowers, Prof. Dr. K. B. Wagener
Chemistry Department, University of Florida
Gainesville, FL 32611-7200 (USA)
E-mail: wagener@chem.ufl.edu
Dr. R. Graf, Prof. Dr. H. W. Spiess
Max-Planck-Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
E-mail: spiess@mpip-mainz.mpq.de

[**] *Published on the occasion of the 25th anniversary of the Max Planck Institute for Polymer Research, Mainz.*
Support by the National Science Foundation under grant DMR-0703261, and by the International Max Planck Research School for Polymer Materials, Mainz is greatly acknowledged. We also thank Dr. Giovanni Rojas for kindly providing the ADMET PE sample.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900377.

^{2}H NMR is well suited for studies of local molecular dynamics exploiting the quadrupolar interaction. The ^{2}H NMR line shapes are very sensitive to segmental motions[7] and can be analyzed by standard available procedures.[7d] Figure 1 shows temperature-dependent ^{2}H NMR spectra for the three polymer samples with deuterated methyl branches. It can be clearly seen that the trend of line shape with temperature is similar for all three cases and shows the gradual build-up of molecular dynamics. At low temperatures, Pake patterns indicative of an axially symmetric tensor with fixed C_3 axes of the branches are observed. With increasing temperature, the singularities of the Pake pattern broaden and the ^{2}H NMR line shape changes via an almost rectangular shape to a pattern resembling an asymmetric tensor (asymmetry parameter $\eta = 1$). As the ^{2}H NMR spectra contain signals from chains in crystalline and noncrystalline regions of the sample, which for the CD_3 groups cannot be separated by the standard procedures,[7a,b] it must be mentioned that such patterns can also result from branches undergoing large-angle motions on intermediate timescales. Upon increasing the temperature further, a rather narrow component in the centre of the spectrum emerges. Remarkably, a regular Pake pattern ($\eta = 0$) with half the static line width in the ^{2}H NMR spectrum is observed only for PE15-CD_3 at $T = 303$ K, indicating the presence of axial rotation sufficiently fast to average the ^{2}H line shape not observed in linear PE itself.[7] Therefore, we attribute this behavior to motions of methyl groups embedded in the crystalline regions. The highly asymmetric ^{2}H line shape observed in all cases is usually interpreted as evidence for a kink motion,[7a,b] but is also consistent with ill-defined rotations around the local chain axis (*all-trans* in the crystallites) with amplitude of about ± 40° (see the Supporting Information).

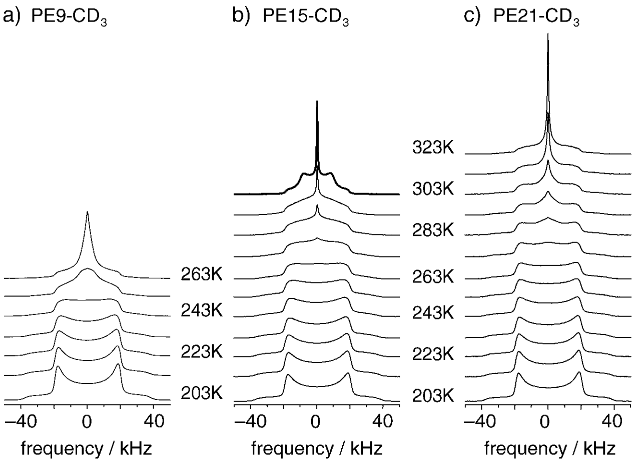


Figure 1. Temperature dependence of ^{2}H NMR spectra for a) PE9-CD_3, b) PE15-CD_3, and c) PE21-CD_3. Acquisition: Bruker Avance 400 MHz NMR spectrometer, quadrupolar echo pulse sequence with echo delay of 30 µs, 90° pulse width of 2.5 µs, recycle delay of 1 s. Samples were heated above their melting points to remove thermal history prior to data collection every 10 K. The special line shape of PE15-CD_3 (b) at $T = 303$ K (bold) indicates the presence of fast axial rotational dynamics.

^{13}C NMR experiments, in which randomly distributed ^{13}C sites are observed along the chain, provide a direct picture of the chain dynamics. The isotropic chemical shift in a magic angle spinning (MAS) NMR spectrum[4] indicates the local conformation[5] and the motionally averaged chemical shift anisotropy (CSA), which can be site-selectively recorded by two-dimensional NMR,[4] reflects local reorientations of CH_2 groups of the polymer backbone. Figure 2 shows both the isotropic and anisotropic chemical shift patterns of the three branched samples and a linear PE sample prepared by ADMET synthesis. The spectra were acquired by separation of undistorted powder patterns by effortless recoupling (SUPER).[9] For linear PE without methyl branches, the ^{13}C isotropic chemical shifts (Figure 2 a) show a strong signal at about 33.5 ppm, which is characteristic of the *all-trans* stems in the orthorhombic phase, a minor monoclinic contribution at around 35 ppm, and a very broad amorphous signal of low intensity at 33–29 ppm. In the following, only the signals originating from the stems in the crystalline regions will be discussed. The ^{13}C static line shape for the orthorhombic signal of ADMET PE exhibits a CSA tensor with $\eta = 0.67$ and principal-axis values of 13 ppm along the chain and 37 ppm and 51 ppm perpendicular to it, as previously discussed in the literature.[10]

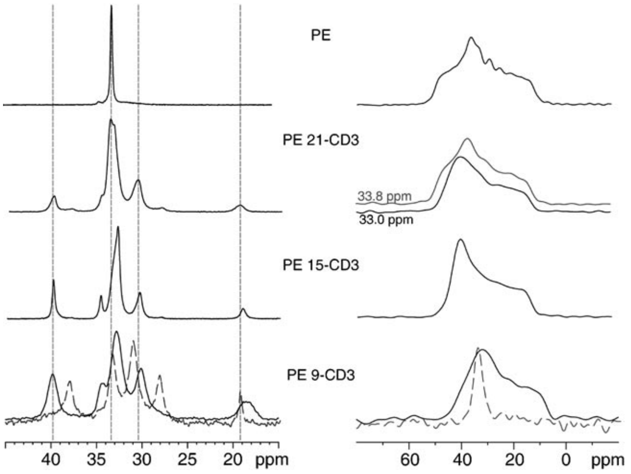


Figure 2. Isotropic (a) and anisotropic (b) ^{13}C NMR chemical shifts for precise polymers. From top to bottom: ADMET PE at 300 K, PE21-CD_3 at 300 K, PE15-CD_3 at 300 K, PE9-CD_3 at 235 K (——) and 245 K (– – –). Spectra were Acquisition: Bruker Avance III NMR spectrometer, 213 MHz ^{13}C Larmor frequency (850 MHz for ^{1}H) using the SUPER[9] pulse sequence; spinning frequency 4125 Hz, initial cross-polarization step to improve ^{13}C spin polarization.

Introducing regularly spaced methyl side groups along the polyethylene backbone changes the morphology[8] and the molecular dynamics. In the ^{13}C MAS NMR spectra (Figure 2), two new signals are observed in all cases, and these are assigned to the methyl (ca. 19 ppm) and the branching (ca. 40 ppm) sites. Moreover, changes are observed for the signals assigned to the regular CH_2 units located in crystalline and noncrystalline regions of the samples along the PE main chain. In PE21-CD_3, the NMR signal at 33.5 ppm, which are known from linear PE and assigned to *all-trans* conformations in the crystalline regions, splits into two signals at 33.6 ppm and 33.2 ppm, which are resolved in our 850 MHz NMR spectrometer. The CSA line shapes for the MAS NMR signal at 33.6 ppm shows a CSA tensor line shape similar to that of PE. The CSA powder line shape of the MAS NMR signal at 33.2 ppm, however, displays the lineshape of an almost axially symmetric CSA tensor, where the principal value of 13 ppm along the crystalline *c* axis persists and the two other values are largely averaged. Remarkably, the averaging observed is consistent with rotations of the *trans* segments around the chain axis, with the same amplitude (±40°) as deduced from ^{2}H NMR for the branch (see the Supporting Information). It should be noted that the isotropic chemical shift of the averaged tensor is shifted by 0.8 ppm towards the *gauche*-containing signals in the noncrystalline regions. As ^{13}C chemical shifts of polymers are sensitive even to small changes in torsional angles,[5b] we assign this small shift to local deviations from the regular *all-trans* geometry resulting from chain twists in the vicinity of the methyl branch. This will minimize the spatial requirements for incorporating the methyl branch in the crystals. The isotropic shift observed actually reflects an average over twisting motions of the defected chain units close to the methyl branch. Finally, the ^{13}C NMR signal at 30 ppm in the spectrum of PE21-CD_3 is assigned to noncrystalline PE. This line is considerably narrower and more intense compared to linear PE. These differences, however, can be attributed to the different crystallinity of the two samples (30% in PE21-CD_3 versus 85% in ADMET PE) and the nonquantitative CP-MAS method used to efficiently record the ^{13}C MAS NMR spectra.

For PE15-CD_3, the signal assigned to CH_2 sites in the crystalline regions is observed at 32.9 ppm with a shoulder at about half the signal height at 33.5 ppm. Remarkably, all ^{13}C signals in the NMR spectrum of PE15-CD_3 show the powder line shape of well-defined axially symmetric CSA tensors; even at 33.5 ppm, the isotropic chemical shift characteristic of undistorted *all-trans* units. Thus, whereas in PE21-CD_3 the CH_2 groups in proximity to the lattice-perturbing methyl branches perform local motions as found in pinned defects, the rotation in PE15-CD_3 at $T = 303$ K involves all the CH_2 groups along a given polymer chain and thus shows collective behavior as in a rotator phase, which was also deduced from X-ray data.[8]

The third sample, PE9-CD_3, with the shortest spacer of only eight CH_2 units between subsequent methyl branches, shows complex structural and dynamic behavior (see the Supporting Information), and will not be used to develop a model for the molecular dynamics in the regular methyl-branched polyethylene samples.

Combining the results for PE15-CD_3 and PE21-CD_3 obtained from ^{2}H and ^{13}C NMR, which probe the branch and the neighboring chain defect separately, we propose a simple model for the molecular dynamics of regular methyl-branched polyethylene in the crystalline regions (Figure 3). In the crystalline regions of PE15-CD_3 and PE21-CD_3, the lattice-perturbing methyl branches undergo axial oscillations around the polymer backbone. In both samples, this motion of the methyl branches increases in amplitude and rate with increasing temperature. However, in the case of PE21-CD_3, this dynamic mode is restricted to CH_2 groups in close proximity to the methyl branch in a twist defect, whereas the CH_2 groups remote from the methyl branches are not involved in this motion as demonstrated by the regular PE CSA pattern observed at 33.6 ppm, but may undergo 180° flips, as known for crystalline PE.[11] The relative intensities of the isotropic lines corresponding to the axially symmetric and the $\eta = 0.67$ CSA pattern is approximately 1:2. From this data, the number of CH_2 units involved in the dynamic twist defect is estimated to be 3–4 CH_2 units on either side of the branch. Based on this picture of a localized dynamic perturbation of the crystal lattice caused by the methyl branches, a 1:1 ratio would be expected between rotating and rigid units for PE15-CD_3. Although MAS NMR signals indicate undistorted *trans* conformers (Figure 3b), all the sites along the chain show similar rotational dynamics. In other words, the localized rotational motion observed in PE21-CD_3 turns into collective dynamics owing to the higher density of defect sites in PE15-CD_3.

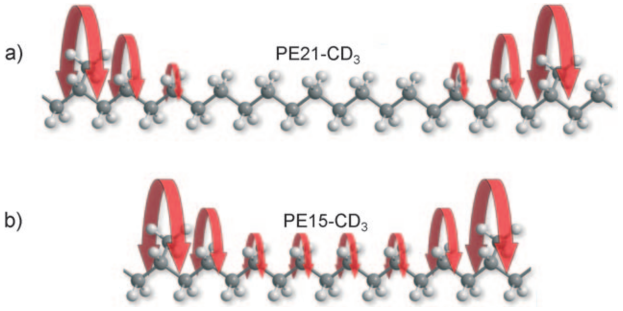


Figure 3. Models for rotational dynamics in a) PE21-CD_3 and b) PE15-CD_3.

The main results of our study can therefore be summarized as follows:

Nature of the motion of the branches: The ^{2}H spectra (Figure 2) clearly show that the branches perform angular restricted rotations reaching amplitudes of about ±40° around the long axis of *all-trans* PE chains close to the melting point.

Influence of the defects on the adjacent chain segments in the same molecule: The methyl branches lead to a twist of the adjacent chain segment (Figure 3), which manifests itself as a component at lower ^{13}C chemical shift. From the intensity of this line relative to that of the *all-trans* segments, the length of the defect is readily estimated to involve about 3–4 CH_2 groups at either side of the branch.

Local vs. cooperative axial motion: The chemical shift anisotropy patterns (Figure 2b) clearly show axial motions of the twisted segments similar to those of the branch itself, whereas the CH_2 groups of the undistorted *all-trans* segments in the sample with long chains between the branches, PE21-CD_3, are rigid on the timescale of these experiments, as in linear PE itself. Thus, the motion of the branches and the adjacent chain defects are localized and can be considered as pinned. In PE15-CD_3, however, the twisted parts are so close that the axial motion imposed by the defect becomes cooperative and also rotates the undistorted *trans* segments in between, as in a rotator phase (Figure 3b).

Incorporation of gauche defects in the crystals: Incorporation of gauche defects is only observed in PE9-CD_3, the sample with the highest branch density, at temperatures close to the melting point.

Reflecting the importance for the mechanical behavior, the nature of chain motions of the stems in the crystals has been under debate for decades. In particular, local conformational defects[1] as opposed to propagating twists[12a] were considered as mechanisms for chain transport. Our results clearly favor twists, which require considerably less disturbance of the crystal lattice. Remarkably, recent NMR studies of chain diffusion between crystalline and noncrystalline regions of linear ultrahigh-molecular-weight PE showed that chain transport, involving cooperative motion of the stems, has a different temperature dependence than the local mobility of the chains. This indicates increased presence of defects that do not transport the chain at higher temperatures.[11] Rotator phases in polymers were deduced from X-ray scattering, thermal analysis, and solid-state ^{29}Si NMR.[12b,c] However, for branched polyethylenes, this is the first time that clear evidence of a rotator phase has been found that is consistent with the results of scattering and microscopy.[8] Our evidence for chain twists also helps to explain the conformational motions of amorphous polymers in the melt, for which two-dimensional NMR has clearly shown that conformational transitions do happen, yet they occur with broad distributions of rotational angles.[13a] This suggests twisted defects in the chain as also considered theoretically.[13b,c] Clearly, the occurrence of both isolated and cooperative motions in stems of single molecules could only be detected by a combination of innovative synthetic chemistry generating well-defined model systems and state-of-the-art solid-state NMR on different nuclei, probing structure and dynamics with different interactions. The implications for polymer physics and engineering of merchandized PE are obvious as irregular branching along the chain[3] results in the possibility of all the different motions identified above to occur in the same polymer.

Received: January 20, 2009

Keywords: defects · molecular dynamics · NMR spectroscopy · polymer branching · polyolefins

---

[1] a) G. Strobl, *The Physics of Polymers*, *2nd ed.*, Springer, Berlin, **1997**; b) B. G. Sumpter, D. W. Noid, G. L. Liang, B. Wunderlich, *Adv. Polym. Sci.* **1994**, *116*, 27–72.

[2] a) C. Piel, P. Starck, J. V. Seppälä, W. Kaminsky, *J. Polym. Sci. Part A* **2006**, *44*, 1600–1612; b) A. Islam, I. A. Hussein, *J. Appl. Polym. Sci.* **2006**, *100*, 5019–5033.

[3] a) R. G. Alamo, J. A. Blanco, P. K. Agarwal, J. C. Randall, *Macromolecules* **2003**, *36*, 1559–1571; b) R. G. Alamo, D. L. VanderHart, M. R. Nyden, L. Mandelkern, *Macromolecules* **2000**, *33*, 6094–6105; c) I. A. Hussein, T. Hameed, M. C. Williams, *J. Appl. Polym. Sci.* **2006**, *102*, 1717–1728.

[4] K. Schmidt-Rohr, H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press, London, **1994**.

[5] a) A. E. Tonelli, *NMR Spectroscopy and Polymer Microstructure*, Wiley-VCH, Weinheim, **1989**; b) R. Born, H. W. Spiess, *Macromolecules* **1995**, *28*, 7785–7795.

[6] a) E. Boz, A. J. Nemeth, K. B. Wagener, K. Jeon, R. Smith, F. Nazirov, M. R. Bockstaller, R. G. Alamo, *Macromolecules* **2008**, *41*, 1647–1653; b) J. A. Smith, K. R. Brzezinska, D. J. Valenti, K. B. Wagener, *Macromolecules* **2000**, *33*, 3781–3794; c) J. C. Sworen, J. A. Smith, J. M. Berg, K. B. Wagener, *J. Am. Chem. Soc.* **2004**, *126*, 11238–11246.

[7] a) H. W. Spiess, *Colloid Polym. Sci.* **1983**, *261*, 193–209; b) D. Hentschel, H. Sillescu, H. W. Spiess, *Macromolecules* **1981**, *14*, 1605–1607; c) M. S. Greenfield, A. D. Ronemus, R. L. Vold, R. R. Vold, P. D. Ellis, T. E. Raidy, *J. Magn. Reson.* **1987**, *72*, 89–107; d) V. Macho, L. Brombacher, H. W. Spiess, *Appl. Magn. Reson.* **2001**, *20*, 405–432.

[8] G. Lieser, G. Wegner, J. A. Smith, K. B. Wagener, *Colloid Polym. Sci.* **2004**, *282*, 773–781.

[9] S. F. Liu, J. D. Mao, K. Schmidt-Rohr, *J. Magn. Reson.* **2002**, *155*, 15–28.

[10] D. L. Vanderhart, *J. Magn. Reson.* **1981**, *44*, 117–125.

[11] a) K. Schmidt-Rohr, H. W. Spiess, *Macromolecules* **1991**, *24*, 5288–5293; b) Y.-F. Yao, R. Graf, H. W. Spiess, D. R. Lippits, S. Rastogi, *Phys. Rev. E* **2007**, *76*, 060801(R); c) Y.-F. Yao, R. Graf, H. W. Spiess, S. Rastogi, *Macromolecules* **2008**, *41*, 2514–2519; d) Y.-F. Yao, R. Graf, H. W. Spiess, S. Rastogi, *Macromol. Rapid Commun.* **2009**, *30*, DOI: 10.1002/marc.200900114.

[12] a) M. Mansfield, R. H. Boyd, *J. Polym. Sci. Part B* **1978**, *16*, 1227–1252; b) E. B. Sirota, A. B. Herhold, *Polymer* **2000**, *41*, 8781–8789; c) H. Kaji, F. Horii, *Macromolecules* **2007**, *40*, 5420–5423.

[13] a) H. W. Spiess, *J. Polym. Sci. Part A* **2004**, *42*, 5031–5044; b) E. Helfand, Z. R. Wasserman, T. A. Weber, J. Skolnick, J. H. Runnels, *J. Chem. Phys.* **1981**, *75*, 4441–4445; c) Y. Y. He, T. R. Lutz, M. D. Ediger, C. Ayyagari, D. Bedrov, G. D. Smith, *Macromolecules* **2004**, *37*, 5032–5039.