Communications to the Editor

NMR Investigation of Chain Folding in Polyethylene Crystals

There is still some controversy as to whether chain folding occurs by adjacent reentry or by random reentry of the chain into the lamella of a polyethylene (PE) crystal.[1] We wish to report some results obtained by application of a new NMR method supplementing the IR[2] and neutron scattering[3,4] methods that have been applied in order to solve this problem. The NMR "deuteron dilution technique"[5] as applied to polymers draws on the H–H dipolar coupling between protons positioned at neighboring stems of a lamellar crystal. On dilution of PE with fully deuterated PED, the intermolecular H–H coupling is replaced by the very small H–D coupling. Thus, one can determine the *intra*molecular H–H coupling by extrapolation to infinite dilution. This "intra" coupling differs for different types of chain folding. It increases in the sequence random reentry, adjacent reentry, molecular clustering, and complete segregation (see below). In practice, the applicability of this idea depends upon the accuracy of differentiating between the "intra" and "inter" contributions to the H–H dipolar coupling. This problem of separating the contributions from various protons in polymer H/D mixtures has been studied in considerable detail,[6] and the results will be published elsewhere.[7] In the present communication, we report our first results in relation to the molecular morphology of solution crystallized PE.

Starting from acetylene, a random mixture of *cis*- and *trans*-CHD=CHD was prepared and polymerized using the soluble $VOCl_3/(C_2H_5)_{1.5}AlCl_{1.5}$ catalyst.[8] The corresponding fully deuterated PED was obtained starting from CD_2Br-CD_2Br (MERCK, Darmstadt). After fractionation, the ratio of the weight and number average molecular weights M_w/M_n was between 2 and 3. Fractions with viscosity average molecular weights of 22 000 and 160 000 (termed L and H in Figure 1) have been used in our NMR experiments. Cocrystallized PEHD/PED samples were obtained from 0.08% xylene solutions at 60 °C.

The ^{1}H-NMR solid echo[9] of the PE samples was recorded with a BRUKER SXP spectrometer at 90 MHz, the signals being accumulated with a DL 905/4000 datalab system. The time distance between the two 90° pulses of the solid echo sequence was $\tau = 10$ μs. The second moment M_2 of the NMR spectrum was obtained by application of a numerical fitting procedure[6] taking into account the fourth order so called $M_{4\epsilon}$ correction.[9] In some test experiments,[10] a pulse distance of $\tau = 5$ μs was used yielding the same M_2 values. By comparison of M_2 and M_4, the fourth moment as measured[10] at $\tau = 5$ μs, we were able to determine the degree of protonation, β =51%, and the crystallinity, α = 87%, the latter in agreement with the X-ray crystallinity.

Below, the experimental M_2 values as determined for the crystalline portion of PE are compared with theoretical values calculated using the crystal structure data of Kavesh and Schultz.[11] We have calculated[7] M_2, M_4, and $M_{4\epsilon}$ of cocrystallized PEHD/PED and PEH/PED, respectively, for the different chain folding models discussed below (Figure 2) taking into account the contributions from residual protons (1.1%) in PED and the proton deuteron coupling. From these calculations, the $M_{4\epsilon}$ correction in

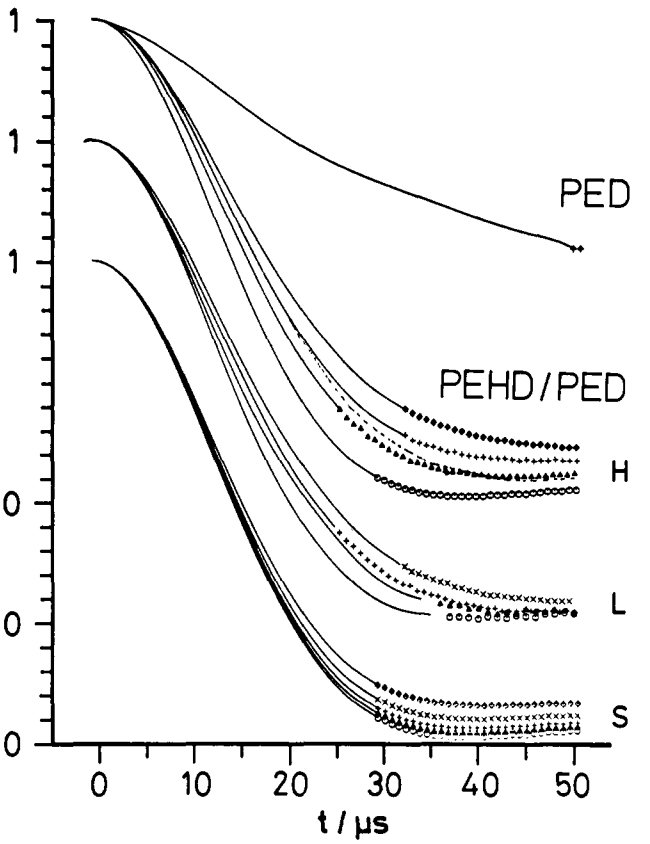

Figure 1. ^{1}H NMR solid echos in cocrystallized PEHD/PED (○, △, +, ×, ◇, respectively): mole ratio x_{HD} = 1.0; 0.6; 0.4; 0.25; 0.15. Full lines are numerical fits of the experimental curves up to the time where the symbols take over. (See text for explanation of H, L, S, and dotted line.) All curves are normalized to one at $t = 0$ and go to zero at $t \to \infty$. Note the vertical shift of the L and H with respect to the S curves.

PEHD amounts to about 10% for a pulse distance of τ = 10 μs and is negligible for $\tau = 5$ μs. On the other hand, the $M_{4\epsilon}$ correction is prohibitively large (about 65%) in normal PEH if $\tau = 10$ μs, and there are higher order contributions to the solid echo. A further reason for doing our NMR experiments with PEHD rather than PEH is that the calculated value of $(M_2^{(\text{intra,adj. reentry})} - M_2^{(\text{intra,random reentry})})/M_2^{(\text{total})}$ is 0.164 for PEHD vs. only 0.097 for PEH.[7] From these considerations we believe that the NMR results reported by Natarajan et al.[12] for cocrystallized PEH/PED are yet insufficient for discriminating between different chain folding models.

In Figure 1, we have shown the solid echos for cocrystallized mixtures of PEHD and PED. The dilution of PEHD with PED has a larger effect on the high (H) than on the low molecular weight (L) samples. For comparison, we have simulated the solid echo signals for the limiting case of completely segregated (S) samples that correspond to a mixture of macroscopic PEHD and PED crystals. These curves have been obtained by simply adding the signals of PEHD and the residual protons of PED with appropriate weight factors. Obviously, the solid echos for our cocrystallized PEHD/PED samples are different from the case of complete segregation. The dotted line in Figure 1 corresponds to a cocrystallized mixture that has been crystallized inadvertently from a 0.13% (instead of 0.08%)

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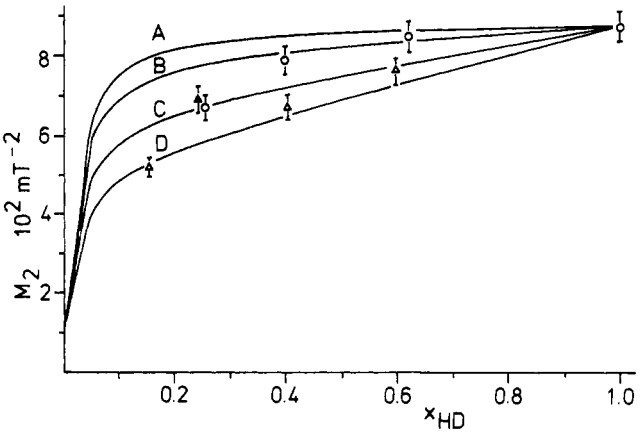

Figure 2. ^{1}H NMR second moments for cocrystallized PEHD/PED. Circles and triangles refer to L and H samples, respectively. Full lines are calculated for the models of complete segregation (A), molecular clustering (B), adjacent reentry (C), and random reentry (D).

xylene solution. The striking influence upon the solid echo may be related to the fact that the random coils start to overlap in this concentration region thus affecting the crystallization kinetics, but this effect needs further investigation.

In Figure 2, M_2 values calculated for four different models of chain folding are compared with experimental M_2's as obtained from the solid echos of Figure 1. Curve A corresponds to the case of "complete segregation" mentioned above. Curve B has been obtained for a cluster model where 80% of the PEHD protons are at the surface (or edge) of a molecular cluster, the other protons inside the cluster having the same second moment as in pure PEHD. Curve C corresponds to chain folding by adjacent reentry along the (110) plane and curve D to the random reentry (or random switchboard[1]) model. The M_2 values of the L samples are close to curve B for the cluster model (see below for $x_{HD} = 0.25$). A "molecular cluster" can be formed by regime II crystallization[13] where a row of PE stems folds back on itself forming a stack of two or more parallel rows. Neutron scattering results have also been interpreted in terms of this superfolding[14] or stacked sheets[15] model. The low value of M_2 at $x_{HD} = 0.25$ (Figure 2) may be due to an isotope effect[14] whereby PEHD grows preferentially at the beginning of the crystallization process causing a gradient of x_{HD} in each crystal. Although this effect should be small at our crystallization temperature of 60 °C and further reduced in PEHD/PED as compared with PEH/PED, it may be nonnegligible at $x_{HD} < 0.3$. Thus, a distribution of x_{HD} about the average $\bar{x}_{HD} = 0.25$ lowers the value of M_2 if we exclude the extreme case of complete segregation where this "distribution" would become singular, and M_2 is given by curve A.

The M_2 values of the H samples are closest to curve D for random reentry if we exclude the value (full triangle in Figure 2) due to the dotted line of Figure 1 (see above). However, further work is necessary in order to discriminate unambiguously between the random and adjacent reentry models. We can qualitatively understand the lower M_2 values of the H as compared to the L samples assuming that the crystallization is diffusion controlled. The entanglement of the high molecular weight chains should then impede the mobility and thus the ability to form adjacent reentry lamellae. It should be noted that there are ~100 stems per molecule in the H series as compared with ~15 stems in the L series.

References and Notes

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Excimer Fluorescence as a Molecular Probe of Polymer Blend Compatibility. 1. Blends of Poly(2-vinylnaphthalene) with Poly(alkyl methacrylates)

As a result of interest in polymer–polymer interactions in the solid state,[1] a number of experimental tools have been employed to study blend compatibility. These include small angle neutron scattering, pulsed nuclear magnetic resonance, optical transmission, density measurement, vapor sorption, calorimetry, dynamic mechanical, and dielectric spectroscopy.[2-8] However, no single technique can answer all questions about interactions at the molecular level. Thus it is desirable to extend the range of methods. One promising approach along these lines has been made recently by Morawetz[9] in a study where nonradiative energy transfer was used as a tool. We present evidence in this paper that another very powerful probe of interaction in physical blends is provided by excimer fluorescence.

An excimer is an excited molecular complex which is formed between two identical aromatic rings, one of which is in a singlet excited state.[10] Three types of nominal excimer forming sites exist in the aromatic vinyl polymers. First, intermolecular interaction between rings on different chains leads to sites which are important in neat homopolymer films and in regions of aggregation in blended systems. The second type results from intramolecular interaction between rings on nonadjacent chain segments; we shall consider it as a subclass of the intermolecular case. A third type which is important in very dilute blends is the intramolecular site formed between aromatic rings on adjacent chain segments. This is of interest because it provides a measure of the population of racemic g^-t and tg^- dyads in syndiotactic sequences and meso tt dyads in isotactic sequences.[11] Experimentally, the population of suitable excimer forming sites is proportional to the ratio of the excimer emission intensity I_D to the emission from the isolated aromatic ring I_M.[11-13] These values are taken

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