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Mixed-Integer and Fractional-Integer Chain Folding in Crystalline Lamellae of Poly(ethylene oxide): A Raman Longitudinal Acoustic Mode Study

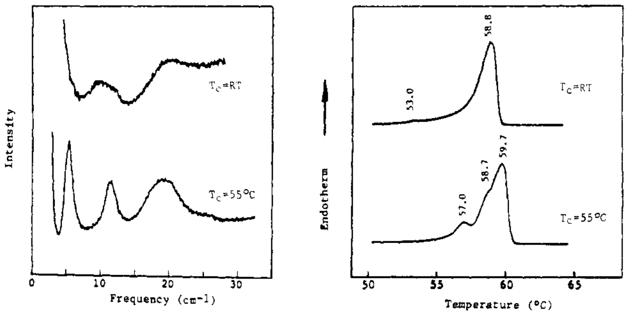
Observations of stepwise increases in SAXS lamellar spacings of low molecular weight poly(ethylene oxide) (PEO) fractions as a function of crystallization temperature[1] and annealing temperature,[2] as well as detailed studies of growth rates and morphologies,[3-6] have led to the concept of integer folds (IF) in these systems, viz., chain folds for which all stems of a molecule are of the same length with chain ends located at the lamellar surfaces. Early Raman longitudinal acoustic mode (LAM) studies of PEO[7] also gave evidence for such IF structures, as have recent transmission electron microscope studies.[8] Similar IF structures have been proposed for ultralong *n*-paraffins.[9]

In all of the above PEO studies, it has been assumed that, for a given polymer and crystallization condition, the lamellae are homogeneous and contain only single IF structures. Our LAM studies of PEO, together with DSC and SAXS data, suggest that there are lamellae that contain a mixture of IF structures as well as lamellae that are comprised of chains with simple fractional-integer folds (FIF). We believe that such FIF are also indicated by results on ultralong *n*-paraffins,[10,11] although the SAXS data[11] were interpreted in terms of general noninteger folds.

The LAM frequency, ν, can be used to determine the ordered length, L, of a polymer chain stem in a crystalline lamella. However, the value obtained for L depends on the assumptions made in relating ν to L: for an unperturbed elastic rod model, $\nu = (1/2L)(E/\rho)^{1/2}$, where E is the elastic modulus and ρ is the density of the rod. For the general perturbed composite elastic rod, more complex relationships hold,[12,13] and if the polymer stem is treated at a molecular rather than a continuum level, the detailed effects of perturbations can be elucidated only by normal mode analyses.[14]

We have refined a force field for PEO that includes intermolecular interactions explicitly and have used it in normal mode calculations of LAM frequencies of extended-chain oligomers.[15,16] We find that, in distinction to the case of planar zigzag polymethylene chains, the LAM of helical chains is affected significantly by lateral interactions. This force field was used to calculate LAM frequencies of folded-chain PEO molecules and to interpret Raman spectra of a series of PEO fractions crystallized under different conditions.[16] Some of these results are presented here.

We consider first the case of a PEO fraction of M = 3000 (M_n = 3336, M_w/M_n = 1.10). In Figure 1 are shown the LAM spectra and DSC curves (obtained at 5 °C/min) for room-temperature crystallization, T_c = RT (RT = room temperature) (crystallization time t_c = 1 day), and T_c = 55 °C (t_c = 5 days) samples. The SAXS patterns of these samples show 3 orders of both a 128-Å and a 107-Å spacing for the T_c = RT sample and at least 6 orders of a 214-Å spacing for the T_c = 55 °C sample. The LAM bands at 5.5 and 11.6 cm^{-1} for the T_c = 55 °C sample correspond to stem lengths of 204-Å (i.e., extended (E)) and 102-Å (i.e., once-folded (F2)) molecules, respectively[16] (the band near 19 cm^{-1}, found in all PEO samples, is a lattice mode[16]). The LAM bands at ~9.5 and 11.6 cm^{-1} for the T_c = RT sample correspond to stem lengths of ~122 and 102 Å, respectively.



(a) (b)

Figure 1. (a) Low-frequency Raman spectra and (b) DSC melting curves of PEO 3000 crystallized at different crystallization temperatures (T_c).

For the T_c = RT sample, the 11.6 cm^{-1} LAM band and the 107-Å SAXS spacing clearly indicate the presence of independent lamellae of once-folded molecules, i.e., monolayer, F2(M), lamellae (the stem length of such chains, assuming a "tight" fold containing three EO units, is expected to be 101 Å). On heating in the DSC, such lamellae (with melting temperature $T_m \cong$ 53 °C[17,18]) are expected to be unstable, and we believe that they convert to bilayer, F2(B), lamellae with observed T_m = 58.8 °C (Figure 1). The other LAM and SAXS spacings, viz., 122 and 128 Å, respectively, are consistent with an F1.5(M) lamella;[16] since the length of the molecule is 211 Å, we presume that in this case the fold is relatively "loose" and that chain ends can emerge from the surface as cilia. Such a lamella would also be expected to be unstable and not show up as a separate peak on heating in the DSC. (We also deduce the presence of FIF chains from an analysis of the LAM spectra of a M = 10 000 PEO sample.[16]) Letting crystallization proceed to t_c = 45 days, we find LAM peaks at 7.5 and 11.6 cm^{-1}, and the 128-Å spacing almost disappears as a 214-Å spacing becomes evident;[16] these changes, plus the DSC scan, can be interpreted in terms of the presence of F1.33(B) and F2(M) chains.[16]

For the T_c = 55 °C sample, the 5.5-cm^{-1} LAM band, the 214-Å SAXS spacing, and the expected 211-Å extended chain length are all consistent with the prescence of E lamellae, as are the T_m of 59.7 °C[17,18] and the T_c[3] (the T_m = 57.0 °C peak in the DSC is probably due to some fractionated species[16]). However, the presence of a LAM peak at 11.6 cm^{-1}, resulting from F2 stems, is not expected at this T_c[3]. The location of such F2 molecules is also not clear; some could be in separate F2(B) lamellae, which is suggested by the shoulder in the DSC at 58.7 °C; however, in view of the relative intensities of the LAM and DSC peaks, we should not exclude the possible presence of F2(B) structures within E lamellae.

We turn now to results on a PEO fraction of M = 5000 (M_n = 4506, M_w/M_n = 1.10). In Figure 2 are shown LAM spectra and DSC curves for T_c = RT, 46 °C, and 58 °C samples, all for t_c = 5 days. The SAXS patterns of these samples show spacings of 136 Å (4 orders), 269 Å (6 orders), and 273 Å (6 orders), respectively. The LAM bands of these samples are at 8.5, 8.7, and 3.9, 8.7, and 13.5 cm^{-1}, respectively, the latter three peaks corresponding to stem

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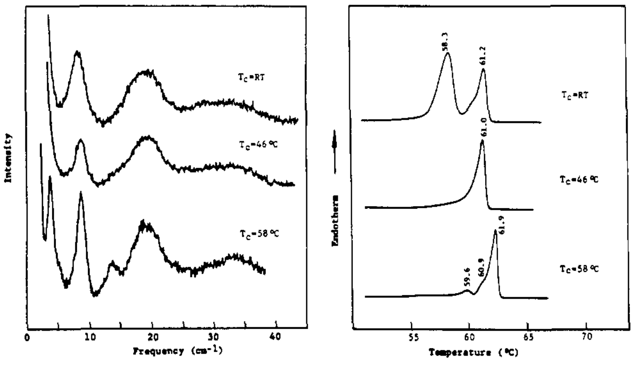

(a) (b)

Figure 2. (a) Low-frequency Raman spectra and (b) DSC melting curves of PEO 5000 crystallized at different crystallization temperatures (T_c).

lengths of 274, 133, and 88 Å, respectively.

For the T_c = RT sample, the LAM band, SAXS spacing, and expected stem length (138 Å) clearly indicate the presence of F2(M) lamellae. The T_m = 58.3 °C peak in the DSC is assignable to this species, with the T_m = 61.2 °C peak being associated with F2(B) structures that develop on heating (at a heating rate of 0.5 °C/min, the lower T_m peak has a very small area compared to the higher T_m peak). For the T_c = 46 °C sample, the LAM peak, SAXS spacing, expected lamellar thickness (~2 × 138 Å), and T_m indicate the presence of F2(B) lamellae. (At a heating rate of 0.5 °C/min, this peak remains single and narrows and is located at the position of the higher T_c = RT peak.) For the T_c = 58 °C sample, the LAM peaks clearly show the presence of E (3.9 cm^{-1}), F2 (8.7 cm^{-1}), and F3 (13.5 cm^{-1}) molecules,[16] the SAXS spacing corresponds to essentially fully extended chains, and T_m = 61.9 °C is that associated with extended chain lamellae[16] (at a heating rate of 0.5 °C/min this peak remains single, narrows, and is 0.6 °C higher than T_m for the T_c = 46 °C sample). In view of the strong F2 LAM band together with an almost negligible F2(B) DSC peak, these results strongly suggest the presence of a single major species consisting of lamellae with E and F2(B) (and probably F3(T)) molecules mixed together.

These, and our other,[16] results thus indicate the existence of folded chain structures more complex than the simple IF lamellae proposed for PEO.[1-6] Our experiments do not, of course, distinguish between structures created initially at T_c and those that may form from these with increasing t_c. In fact, the M = 3000 results mentioned above clearly show the effect of t_c at T_c = RT, and comparable changes are seen with t_c for the M = 5000 sample at T_c = RT.[16] For both samples, however, prolonged annealing near the melting point does not eliminate the F2 LAM peak, leading to the possibility that pure E lamellae are not trivial to prepare.

The above conclusions could be confidently derived from the Raman spectra of PEO as a result of our normal mode analyses of the LAM in this helical polymer.[16] We plan to apply these insights to more detailed studies of the crystallization and annealing processes in this polymer.

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New Ring-Opening Polymerization via a π-Allyl Complex. 1. Polymerization of Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate Catalyzed by a Palladium(0) Complex

Palladium complexes catalyze a wide variety of useful synthetic reactions.[1] It is attractive and interesting to try to introduce some of these reactions into the field of polymerization chemistry. This communication deals with the new ring-opening polymerization of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1) in the presence of a Pd(0) complex (Scheme I).[2]

In organic synthesis, 1 is known to react in the presence of Pd(0) catalyst with some nucleophiles such as secondary amines[3] and active methylene compounds[4] as well as with electron-deficient olefins such as methyl acrylate[5] (Scheme II). The key intermediate of these reactions is a π-allyl complex, 2, which has two electrophilic sites and one nucleophilic site. It resembles zwitterionic intermediates having an electrophilic site and a nucleophilic one, which have conveniently been polymerized by a mechanism of the so-called "No Catalyst Copolymerization".[6] A speculation on the basis of the combination of this polymerization chemistry with the above organic synthesis involving π-allyl Pd complex[1,7] has brought about a new type of ring-opening polymerization of the present paper. It has been found that the binary system of a catalytic amount of a Pd(0) complex and an initiator such as diethyl malonate induces the ring-opening polymerization of a monomer, 1 (Scheme I).

The structure of the product polymer, 3, was established by spectroscopic analysis, which is identical with that of the polymer produced by free-radical ring-opening polymerization.[8] A typical procedure for the polymerization was as follows. $Pd_2(dba)_3 \cdot CHCl_3$ (2.4 mg, 2.3 × 10^{-3} mmol, dba, dibenzylideneacetone) and 1,2-bis(diphenylphosphino)ethane (dppe, 1.8 mg, 4.5 × 10^{-3} mmol) were stirred in dry CH_3CN (0.8 mL) under argon atmosphere at room temperature for a while. The color changed from

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