Notes

Relation between Steric Factors and External Degrees of Freedom

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Chain flexibility of polymers is characterized by two different quantities: the steric factor, obtained from viscometry and from geometrical considerations of the polymer chain, and the number of external degrees of freedom, obtained from volumetric data for polymers. However, these two characterizations of flexibility obtained from different experimental data are not necessarily the same. The purpose of this note is to examine a simple relationship between these two flexibility parameters.

For an unperturbed chain, the steric factor σ is defined by

$$\sigma \equiv (\langle r_0^2 \rangle / \langle r_f^2 \rangle)^{1/2} \tag{1}$$

where $\langle r_0^2 \rangle$ and $\langle r_f^2 \rangle$ are respectively the mean-square end-to-end distances of a chain and of a model chain with fixed valence angles but with completely free internal rotations. Therefore, σ gives a measure of the hindrance to internal rotations about the main bonds of the chain; σ is equal to 1 for chains with free rotations and $\sigma > 1$ for chains with hindered internal rotations. The values of σ obtained from θ-solvent experiments have been tabulated by various authors.[1-3]

The other flexibility factor, the number of external degrees of freedom $3c$, has been discussed by Prigogine,[4] Flory,[5] and others in conjunction with the equation-of-state theory for amorphous polymers and polymer solutions.

To relate $3c$ to σ, we assume that a polymer molecule can be represented by a flexible, linear chain of r point centers where r is given by

$$r = mn \tag{2}$$

where m = number of main chain bonds in each repeating unit and n = number of repeating units in the chain.

This assumed linear chain has $r - 1$ stretching vibrations, $r - 2$ bending vibrations, and $r - 3$ internal rotations, also called twisting vibrations.[6]

In addition to these, it has three translations and three rotations around its center of mass.

The frequencies of stretching and bending vibrations are such that their contribution to chain flexibility is minimal when compared with the contribution of twisting vibrations. Therefore it can be assumed for most polymers that $r - 1$ stretching and $r - 2$ bending vibrations are density independent and do not contribute to $3c$. This assumption leaves $r - 3$ degrees of freedom. Some, or possibly all, of these may be density dependent.

Since σ is a measure of the hindrance to internal rotations, $1/\sigma$ gives the relative flexibility of the polymer chain. To relate σ to $3c$, the simplest assumption is that only $(r - 3)/\sigma$ of the twisting vibrations have low enough frequencies (or high enough amplitudes) to be affected by intermolecular forces. These vibrations, therefore, are density dependent. The total number of external degrees of freedom per molecule is then given by

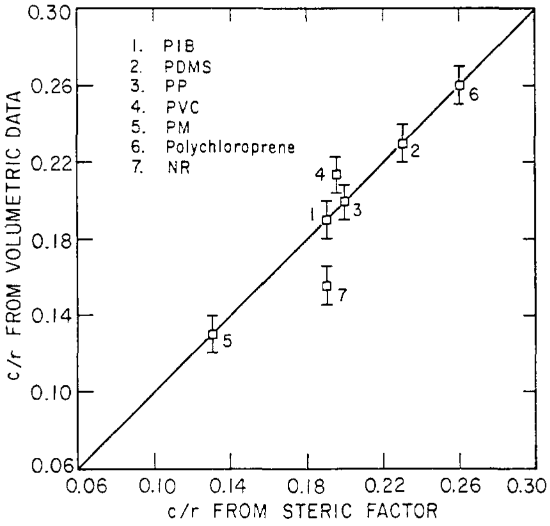

Figure 1. Comparison of c/r from volumetric data with c/r from steric factor. Results for PS and PEO are omitted as discussed in the text. PIB is polyisobutylene, PDMS is poly(dimethylsiloxane), PP is polypropylene, PVC is poly(vinyl chloride), PM is polymethylene, NR is natural rubber.

$$3c = [(r - 3)/\sigma] + 6 \tag{3}$$

Strictly, eq 3 gives only a lower bound for the number of external degrees of freedom since the contributions of stretching and bending vibrations are not taken into account.

The equation of state theory gives[7]

$$c/r = P^* V_{\text{sp}}^* (M_0/m)/RT^* \tag{4}$$

where P^*, V^*_{sp}, and T^* are the reducing parameters, M_0 is the weight of the repeating unit, and R is the gas constant.

Parameters P^*, V^*_{sp}, and T^* from volumetric data were reported by several authors.[8-11] To compare numerical values of c/r from eq 4 with those obtained from eq 3, we divide eq 3 by r and take the limit as r goes to infinity

$$\lim_{r \to \infty} c/r = 1/3\sigma \tag{5}$$

Figure 1 compares the number of external degrees of freedom calculated from eq 4 to those calculated from eq 5. Vertical bars in Figure 1 indicate estimated experimental uncertainties in volumetric data. There are also appreciable uncertainties in σ but these are not shown in the figure. Figure 1 indicates that eq 5 predicts c/r for PIB, PDMS, PP, PVC, PM, poly(chloroprene), and natural rubber within the reported variations in σ and within the accuracy of the volumetric data. Disagreement for the PEO is in the direction opposite to that which we expect. Dondos and Benoit[12] have pointed out the influence of solvents on σ and have shown that σ can vary considerably, especially for polar polymers.

The disagreement for PS is in the right direction since eq 5 gives only a lower bound for c/r. The additional density-dependent contributions from bending and stretching vibrations and the low-frequency vibrations due to the motion of flexible side groups are not taken into account in eq 5.

The results reported here suggest a relation between the number of external degrees of freedom as found from volumetric data with that calculated from the steric factor. Since σ values obtained with different experimental methods and in different theta solvents show significant variations, only semiquantitative significance can be assigned to eq 5.

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Mixed-Crystal Infrared Study of Chain Organization in Polyethylene Crystallized under Orientation and Pressure

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When high-density polyethylene (PEH) is crystallized under certain conditions of orientation and high pressure, for example, by extrusion from an Instron capillary rheometer, samples (which we will refer to as capillary extruded PEH) are obtained which have unusual physical properties.[2a] It has been suggested,[2a] primarily on the basis of melting point data[2a] and X-ray[2b] and electron diffraction patterns,[3] that extended chain structures exist in such specimens, and that they account for the different physical properties. The above, as well as other, techniques of characterization provide, however, only an indirect inference of the kind of chain organization in such polymer samples. The object of the present study was to determine the nature of the chain organization by the more direct method of mixed-crystal infrared spectroscopy.

Theoretical[4,5] and experimental[6,7] studies have shown that the infrared spectra of mixed crystals of PEH and poly(ethylene-d_4) (PED) can be used to identify the relative location of portions of the same chain within a polyethylene crystal. This means that the pattern of chain folding in the crystal can be identified.[6] If folding does not occur, but the chains crystallize in their fully extended state, then the infrared spectra of such mixed crystals exhibit predictably different features. We have studied the infrared spectra of extruded samples of PEH containing, for optimization of the technique,[7] small amounts of PED. The spectra of such mixed-crystal systems indicate that extended chain morphology can predominate in capillary extruded polyethylene.

Table I
Infrared Splittings (in cm^{-1}) for Capillary Extruded Polyethylenes

Sample	$\Delta\nu_b(CD_2)$	$\Delta\nu_r(CH_2)$
Marlex 6009 plug		$10.9_5 \pm 0.1$
Marlex 6009 strand		10.9_5
PEH–PED (10:1) S.C.[a]	5.4 ± 0.15	10.4
PEH–PED (10:1) M.C.[b]	0[c]	10.4_5
PEH–PED (10:1) plug	0[d]	10.4
PEH–PED (10:1) strand	0[e]	9.9_8
$C_{36}H_{74}$–$C_{36}D_{74}$ (10:1)[f]	0[g]	9.9_3

[a] S.C. = single crystals; T_{xl} = 55°. [b] M.C. = melt crystallized; single crystals heated to 150° for 24 hr and cooled to room temperature. [c] $\nu_b = 1089.0 \pm 0.2$ cm^{-1}. [d] $\nu_b = 1088.8 \pm 0.2$ cm^{-1}. [e] $\nu_b = 1089.0 \pm 0.2$ cm^{-1}. [f] Cast at room temperature and then melted at 80° for 3 hr. [g] $\nu_b = 1088.7 \pm 0.2$ cm^{-1}.

Experimental Section

The polymers used in this study were a Marlex 6009 PEH ($M_w \cong 155{,}000$) and a Volk Radiochemical Co. PED ($M_w \cong 245{,}000$), the same materials used in earlier work.[6,7] The mixed-crystal samples were PEH-PED (10:1) on a molar basis. The material used in the Instron was either Marlex 6009 or single crystals of 10:1 PEH-PED prepared by cocrystallization of the two polymers from dilute xylene solution, the crystallization temperature being 55°. (The latter procedure was used in order to ensure an initially mixed sample.[6])

Specimens were prepared as follows. The barrel of the Instron rheometer was charged with polymer and maintained at 160° for 1 hr under a force of about 6 lb on the ram. The temperature was then allowed to drop slowly to 136° with about 2 lb of ram force. The melt was then extruded at a shear rate of 0.3 sec^{-1} until a steady force was obtained. The force was then removed, and when the stress reached zero the extrusion procedure was repeated. The attainment of the same steady-state values of the force suggests that complete melting of the polymer sample was attained. At this point the rate of shear was increased abruptly to 15 sec^{-1}. The pressure increased rapidly, and was maintained at about 2400 atm for 20 min. The temperature was then allowed to drop to 110° at about 0.5°/min while maintaining the pressure at 2400 atm. At this point the pressure was released and the extrudate was removed from the capillary. The capillary had a length of 2.000 in. and a diameter of 0.050 in.

The final sample consisted of a thin relatively transparent strand (which derived from the capillary region of the die) attached to a thick opaque plug (which came from the rheometer barrel). X-Ray diffraction patterns showed the strand to have very high axial chain orientation, as previously reported,[2a] whereas the plug exhibited no orientation. All experiments involving the strand were performed on the very highly oriented portion immediately adjacent to the plug.

Melting points were determined using a differential scanning calorimeter cell in a DuPont 900 thermal analyzer operating at 10°/min. The melting points for the plug and strand were 134 and 140°, respectively, for the Marlex 6009, and 133 and 140°, respectively, for the mixed-crystal specimen. X-Ray diffraction patterns, taken with a mirror-monochromator Guinier focusing camera employing Cu Kα_1 radiation and a 127-mm specimen-to-film distance, showed that the (110) and (200) spacings were respectively identical in the plug and strand of both Marlex 6009 and the mixed-crystal sample. Thus, the orthorhombic unit cell dimensions are unaffected by the different physical treatment or the cocrystallization with PED. Infrared spectra were obtained on a Perkin-Elmer Model 180 spectrophotometer, using ~3-mil thick sections from the plug and the strand. The spectral observations