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Monte-Carlo Calculation

Unperturbed and Solvent Modified Unperturbed Dimensions of Macromolecules via NMR-Data on Low Molecular Weight Models

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Herrn Professor Dr. Dr. h. c. Mult. Herman F. Mark
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Summary

A novel approach is proposed to derive the temperature dependent unperturbed dimensions of macromolecules as well as the influence of solvent action on these dimensions: The populations of conformers are analyzed by NMR using low molecular weight analogs in the respective milieu. The microconformers are summed up to yield the macroconformation, applying Monte-Carlo calculation. Because long distance interactions are nonexisting in the conformational balance of those models, the macrodimensions derived in this way are the unperturbed ones, with and without specific solvent influence, depending on the choosen solvent and temperature.

Studies have been carried out using ditactic unpolar head-to-head poly(propylene)s as well as polar head-to-head poly(vinylchloride)s and chlorinated poly(octenamer)s, respectively. Comparison with viscosity and light scattering data prove that for head-to-head poly(vinylchloride)s the dependence of the solvent modified unperturbed dimensions on configuration has identical tendency for calculated and measured data.

As an unique consequence of the solvent action it has been derived from the NMR studies on the low molecular weight models for erythrodiisotactic poly(vinylchloride) that the short range interaction of polar solvents decreases the solvent modified unperturbed macrodimensions when compared with those in a virtually non-interacting milieu. Separation of short from long range influences on the expansion factor appears to be realizable by the discussed approach.

Solvent modified unperturbed dimensions are discussed in connection with dimensions of macromolecules in the θ-state, in semidilute and in plasticized systems and in compatible polymer blends.

Introduction

The dimensions of macromolecular chains are influencing the properties of polymers both in solution and in bulk in a dominant manner. In this connection the unperturbed dimensions play a role first from the theoretical standpoint, because they are free from long range interactions. As theoretically predicted by Flory [1] and verified by neutron scattering studies macromolecules exhibit their unperturbed dimensions also in the melt, in the glassy state and in concentrated solutions.

Specific solvent action should influence, however, the dimensions of polar macromolecules in concentrated solutions. Recent NMR investigations on polar low molecular weight compounds prove that the conformational balance may be strongly altered by solvent action: Trans-1,2-dichlorocyclohexane exhibits biaxial conformation dominantly in unpolar solvents, whereas in polar solvents the biequatorial conformation is preferred, which is also the arrangement in the crystalline state [2]. Analog linear compounds show similar effects. Because the macromolecules are built up by sequences of such subunits, the unperturbed macrodimensions should depend on the solvent even in concentrated solutions of polar polymers.

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Unperturbed dimensions may be derived from RIS calculations [3] with certain limitations due to adjustable molecular parameters. Experimentally they may be determined in Θ-solutions [4] directly or by extrapolation of measurements in thermodynamically good solvents [5]. It has to be noted, however, that dependences of such dimensions on the respective solvent systems have been found. In any case the pseudoideal state appears to be disturbed with respect to the conformation at a segmental level: The Θ-state is built up by the competing long range effects, the excluded volume, which expands the coil, and the polymer-polymer interactions, which contract the coil.

Solvent induced effects on unperturbed dimensions are not accessible up to now by the RIS approach, which should take into consideration the solvent action on the conformational balance.

Neutron scattering should be capable to detect this effect by measurements in concentrated solutions. There are no relevant studies performed up to now, however, to our knowledge. Studies on compatible polymer blends - deuterated poly(styrene) / poly(vinylmethylether) - by neutron scattering have demonstrated that the energetic interaction beetween the macromolecular components is expanding the coil dimensions of the poly(styrene) [6]. The conformation of the monomeric subunits is not accessible, however, in this way. NMR seems to be the mostly promising method for an analysis of the influence of the solvent on the conformation at a segmental level. In the present paper we try to demonstrate that unperturbed dimensions and solvent modified unperturbed dimensions of macromolecules may be derived from the NMR data too.

Results and Discussion

In previous papers [7] [8] [2] the dependence of the populations of conformers has been described for the methine-methine bond in ditactic head-to-head poly(propylene)s. This has been effected by ^{13}C-NMR measurements on low molecular models, which exhibit conformational balance identical with the respective polymers. Their chemical shift under fast exchange conditions, δ, is the consequence of the populations, p_i, and the chemical shifts, δ_i, of the coexisting rotamers:

$$\delta = \sum_{i=1}^{n} p_i \delta_i \qquad (1)$$

The shifts of the rotamers have been determined at low temperatures under slow exchange conditions. The shift differences are in the order of ppm's due to the γ-effect occuring for gauche conformations. The populations of the rotamers are correlated with the respective energy differences, ε_i, m_i being the number of the respective rotamers:

$$p_i = m_i \exp(-\varepsilon_i/kT) \Big/ \sum_{i=1}^{n} m_i \exp(-\varepsilon_i/kT) \qquad (2)$$

The measurements have been carried out in virtually non-interacting solvents for both the polymers and the low M. W. models. In any case solvatation of unpolar molecules is practically not depending on the solvent because of the lack of specific interactions.

The situation is different for polar polymers, i. e. ditactic head-to-head poly(vinylchloride)s and their low molecular weight analogs, as discussed in the introduction. The NMR patterns for the polar chloro compounds may be concluded from considerations derived from the experiments on the unpolar methyl substituted ones, as described before [2]. It turns out that the preferred conformations differ for both the types of compounds: Methyl groups prefer to be situated in gauche conformations, whereas Cl-groups prefer anti (Figure 1). The chemical shifts for a low molecular weight model for threo type head-to-head poly(vinylchloride), d,l-2,3-dichlorobutane, versus 1/T are shown in Figure 2. It is evident that the data recorded on the d,l-compound under fast exchange conditions exhibit a different tendency for propane, the unpolar solvent, and for chloroform, the polar one: In propane gauche$^+$ is preferred, in chloroform gauche$^-$. In the meso-configuration anti is favoured in the unpolar milieu. Polar solvents induce a tendency towards gauche.

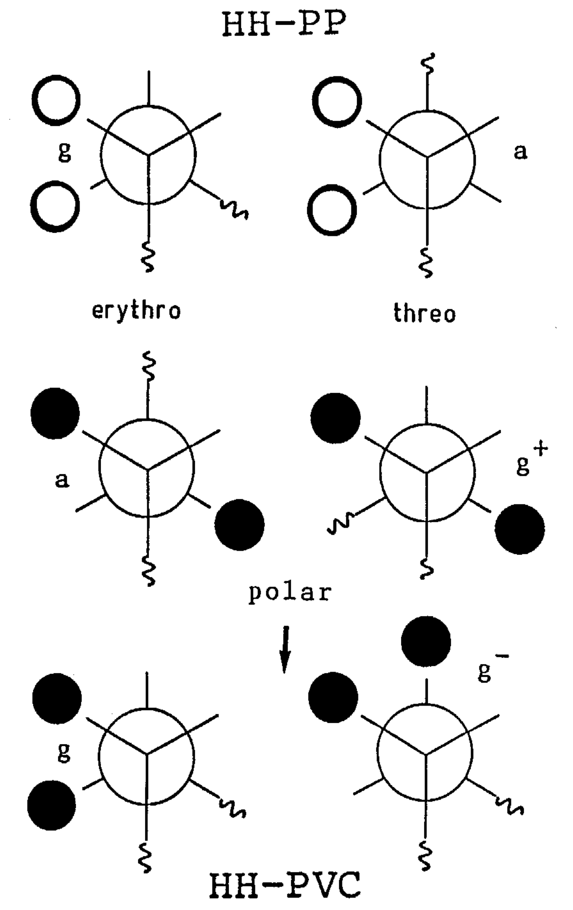

Figure 1 : Lowest energy rotamers. Head : erythro- and threo-type head-to-head poly(propylene)s. Middle : erythro- and threo-type head-to-head poly(vinylchloride)s. Bottom: HH-PVC - conformational influence of polar solvents

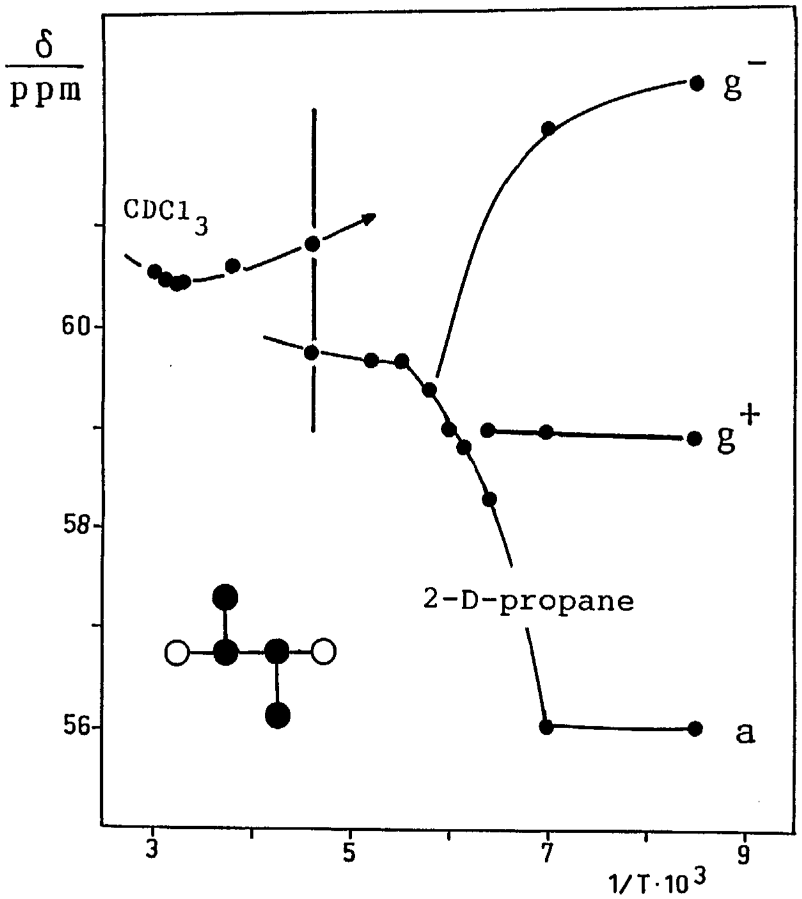

Figure 2 : Fast and slow exchange ^{13}C-NMR spectra of d,l-2,3- dichlorobutane, chem. shift versus 1/T. Solvents: 2-D-propane and $CDCl_3$

Before presenting our approach to calculate macro- from microconformations we like to discuss and to modify the concept of perturbed and unperturbed dimensions of macromolecules. For C-C chains the unperturbed dimensions, $<r^2>_o$, are correlated with the dimensions based on free rotation around the valence angle, θ, $<r^2>_{of}$,

$$<r^2>_{of} = nl^2 (1 - \cos\theta) / (1 + \cos\theta) \qquad (3)$$

through the hindrance parameter σ (ϕ the torsion angle)

$$\sigma^2 = (1 - <\cos\phi>) / (1 + <\cos\phi>) \qquad (4)$$

$$<r^2>_o = \sigma^2 <r^2>_{of} \qquad (5)$$

The perturbed dimensions, $<r^2>$, are expanded by a factor α:

$$<r^2> = \alpha^2 <r^2>_o = \alpha^2 \sigma^2 <r^2>_{of} \qquad (6)$$

In the expansion factor three components are comprehended, excluded volume, polymer-solvent and polymer-polymer interaction. All of them are interpreted as long range interactions commonly. Effectively the solvent-polymer interaction is of short range type, however, which occurs with low molecular weight compounds also, as demonstrated clearly by NMR data. Therefore, we may split up in components, with the indices $_{ev}$ for excluded volume, $_{12}$ for polymer-solvent and $_{22}$ for polymer-polymer interaction:

$$<r^2>^{1/2} = \alpha_{ev} \alpha_{22} \alpha_{12} \sigma <r^2>_{of}^{1/2} \qquad (7)$$

Taking into consideration that α_{12} may be accessible via NMR data of low molecular weight compounds in an interacting solvent, we define a solvent modified hindrance parameter, σ_s:

$$\sigma_s = \alpha_{12} \sigma = \alpha\sigma / \alpha_{ev} \alpha_{22} \qquad (8)$$

The order of magnitude for the two long range components of α is around 2 for α_{ev} and < 1 for α_{22}. Both are effective for macromolecular chains only. α_{12} is not necessarily >1, as it will be demonstrated in the following by NMR measurements on low molecular weight model compounds.

In consequence of the fact that long range interactions are non-existing in low molecular weight models for macromolecules the chance is offered to sum up their conformers by a Monte-Carlo calculation to yield the unperturbed dimensions, $<r^2>_o$, as well as the solvent modified ones, $<r^2>_s$, of the respective macromolecules. Solvent modified unperturbed dimensions are not accessible up to now by the RIS approach, because the solvent action on the conformational balance cannot be taken into account in an appropriate way. These dimensions may be very usefull, however, to understand solvent dependent effects in polymer systems as discussed below.

In the Monte-Carlo calculation the contributions of the rotamers around the methine-methine bonds as determined by NMR analysis of the respective low molecular weight models are inserted, whereas those for the methylene-methylene bond have been assumed to reflect the situation in poly(ethylene). For the methylene-methine bond an energy difference of 1.0 kJ between gauche and anti has been assumed. In a first approximation, the torsion angles have been supposed to be the undistorted ones, 60^o and 300^o for the gauche and 180^o for the anti conformers. Calculations have been carried out for head-to-head poly(propylene)s and poly(vinylchloride)s, with erythro and threo configuration as well as for a statistical 1:1 mixture of both of them, in n-pentane and, for the hh-PVC's, in THF additionally. The details of the calculation procedure will be published elsewhere [9].

Figure 3 gives the comparison of the results for both the polymer types in n-pentane. Assuming that due to the lack of specific interaction unperturbed data are yielded, the hindrance factor σ is plotted versus erythro-threo ratio and temperature.

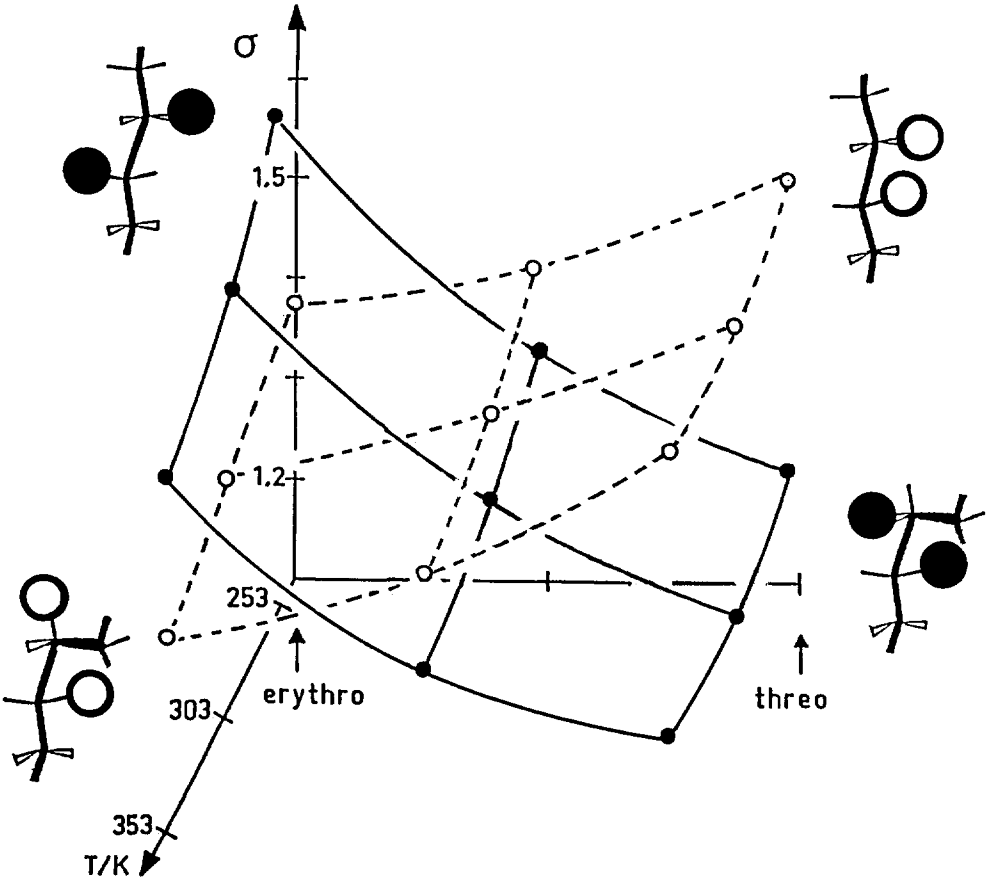

Figure 3 : Monte-Carlo calculation of the unperturbed hindrance factor, σ , for head-to-head poly(propylene)s, O ---- , and poly(vinylchloride)s, ● —— , versus erythro-threo content and temperature. Solvent: n-pentane
Lowest energy conformers for erythro and threo chains visualized

The influences of tacticity as well as of the polarity of the macromolecular chains are much more dominant than the temperature influence on the hindrance factor and the unperturbed dimensions, consequently. In accordance with the situation visualized in Figure 1 the threo head-to-head poly(propylene)s favour the all-anti conformation, whereas the erythro chain prefers a gauche kink with the consequence of smaller unperturbed dimensions. For the corresponding head-to-head poly(vinylchloride)s the situation is just inverse, as a consequence of the polarity of the substituents. It seems to be strange, at a first view, to discuss unperturbed dimensions of poly(vinylchloride)s in an actual non-solvent. The point is that the lack of solubility is a consequence of polymer-polymer interaction (α_{22}) exclusively. The unperturbed dimensions of the polar erythro macromolecule are significantly greater than those of the respective unpolar one.

In Figure 4 the situation is compared for head-to-head poly(vinylchloride)s in the unpolar n-pentane and in the polar THF. For erythro-type chains the unperturbed hindrance factor exceeds the solvent modified one: In THF the chain has more gauche tendency than in n-pentane. Under specific solvent action the coil has the tendency to shrink, when polymer-polymer interaction is not taken into consideration. Because THF is a

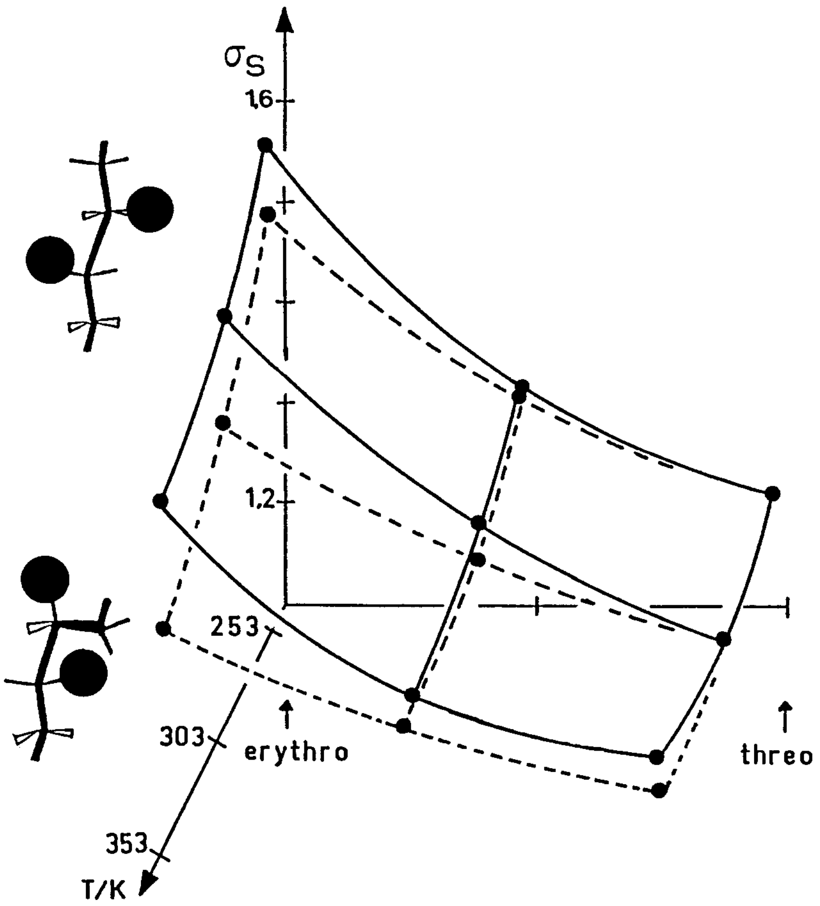

Figure 4 : Monte-Carlo calculation of the unperturbed hindrance factor, σ ● ——, and the solvent modified hindrance factor, σ_S ● ----, for head-to-head poly(vinylchloride)s, versus erythro-threo content and temperature
Solvents: n-pentane and THF. Lowest energy conformers visualized

thermodynamically good solvent, polymer-polymer interaction is suppressed, and the perturbed dimension are high. For the threo type head-to-head poly(vinylchloride) hindrance factors and unperturbed dimensions are nearly invariant with respect to the polarity. This is a consequence of the fact that polar interaction induces preference of gauche-kinks when compared with the gauche$^+$ tendency in unpolar milieu, without significant influence on the macroconformation. It is evident too that the average sequence lenght of anti conformers has to be relatively high in order to generate significant effects on the coil size: In 1:1 erythro-threo chains one observes minor differences between the unperturbed and the solvent modified dimensions only.

In Figure 5 the Monte-Carlo data for the unperturbed hindrance factor, σ, are compared with those measured by light scattering and solution viscosity 5) (own measurements and literature data 10)). Additionally the computed data for the THF modified hindrance factor, σ_S, are plotted. Calculated and measured values have identical tendency. This indicates that the proposed approach takes into consideration configurational and conformational influences in a correct way. The experimental data are higher, indeed, by a factor 1.7 to 1.9. This is an effect, which uccurs generally in a similar way when determining unperturbed dimensions by RIS calculations. Some reasons for the systemat-

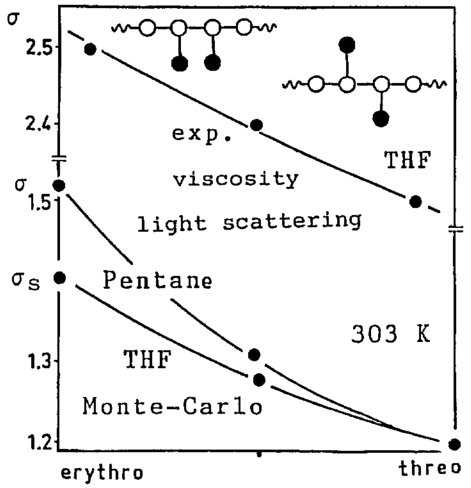

Figure 5 : Hindrance factor for head-to-head PVC, σ experimental and calculated, σ_S in THF, calculated

ical deviations may be discussed shortly. First, the probability of identical sense gauche conformers is overestimated in the calculations, as it is well known for poly(ethylene), i. e. Second, influence of the next neigboured subunit is not taken into consideration in our calculations. For head-to-head chains this should be tolerable, however, especially for the chlorinated poly(octenamer)s, which will be discussed later. Here the head-to-head groups are decoupled by the long methylene sequence. Third, the torsion angle for gauche deviates significantly, which is proven by force field calculations [11] and by NMR measurements [12] on dimethylbutane. Forth, the admitted energy difference for the methylene-methine rotamers may be not exact. Work is in progress to take into account the discussed effects in our Monte-Carlo calculation. Tail-to-tail low M. W. models will be synthesized in this connection.

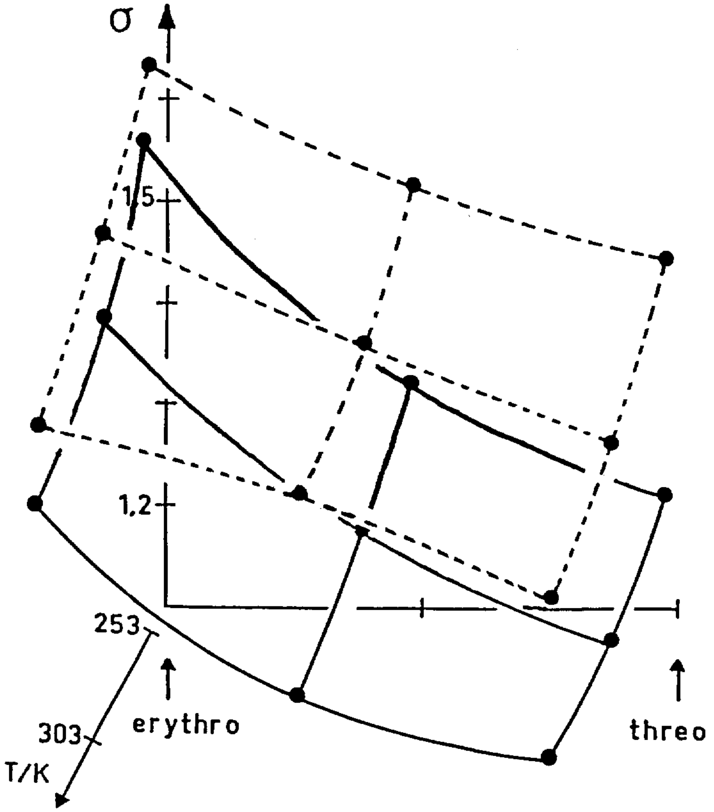

Figure 6 : Monte-Carlo calculation of the unperturbed hindrance factor, σ ● —— for head-to-head poly(vinylchloride)s and ● ---- for chlorinated poly(octenamer)s, versus erythro-threo content and temperature. Solvent: n-pentane

By chlorination of high-cis and high-trans poly(octenamer)s one gets polar head-to-head macromolecules, which exhibit six methylenes per subunit. Assignment of the conformers is possible here by direct solid state NMR analysis of the polymer [13]. Figure 6 compares the unperturbed hindrance factor of those polymers with that of the head-to-head poly(vinylchloride)s. As expected the dependence of σ on the configuaration is flatter for the chlorinated poly(octenamer)s, and the dimensions are greater.

In conclusion, the concept proposed for the determination of macroconformations from experimental data of the microconformations as derived from low molecular weight analogs seems to be a promising one. Solvent modified unperturbed dimensions may offer new insights into the complex phenomena occuring by solvatation of macromolecules, because long and short range influences are separated:

- The Θ-state may be understood better on a molecular base, especially concerning solvent influences on the unperturbed dimensions.
- Solvent effects on the dimensions in semidilute solutions may be investigated.
- In plasticized systems conformational analysis is possible not only with respect to the macromolecules, but for the plasticizer molecules also.
- In compatible blends conformational analysis of both the interacting macromolecular components may be realizable.

Generally the proposed approach may be developped further in order to derive unperturbed and solvent modified unperturbed dimensions of macromolecules on the base of experimental data on low molecular weight analogs exclusively.

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