

UNPERTURBED AND SOLVENT MODIFIED UNPERTURBED DIMENSIONS OF MACROMOLECULES VIA NMR – DATA ON LOW MOLECULAR WEIGHT MODELS

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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 nonexistent 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 chosen 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

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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 crythrodiisotactic 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.

OSMOSEDIMENTATION: ANALYTICAL AND PREPARATIVE USES

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Sedimentation equilibrium is approached faster if the solution under study is allowed to settle in a dialysis cell, in contact with pure solvent through a semi-permeable membrane.

This phenomenon (osmosedimentation) has been studied in this laboratory, using both theoretical and experimental approaches. Theoretically, it can be understood by using Rayleigh's dissipation function of irreversible thermodynamics. Onsager's formalism leads to some relationships showing that sedimentation coefficients may increase by two or three orders of magnitude, in osmosedimentation experiments.

To this point, osmosedimentation has been successfully used to:

- i) – concentrate polymer lattices (under gravity) and polymer solutes (low-speed centrifugation);
- ii) – determine solute polymer and colloidal particle M_w , M_z and virial coefficients, both under gravity and low speeds;
- iii) – evaluate dispersed particle electrical charge;
- iv) – generate concentration gradients, useful for cell fractionation, at low centrifugation speeds.

From the results obtained we conclude that this is a powerful, low-cost technique, which may be useful in a number of polymer chemistry problems.

ISOCHRONE VISCOELASTIC FUNCTIONS VIA ACTIVATION ENERGY OF FLOW – CHARGE TRANSFER COMPATIBILIZED POLYBLENDS

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SYNOPSIS

It is shown that charge transfer interaction in polymer systems enlarges the rubber plateau and contributes to stabilization of incompatible polymer blends.

1. BACKGROUND TO THE ACTIVATION ENERGY OF FLOW

Based on Boltzmann's superposition principle viscoelastic functions are expressed in terms of the relaxation