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Flory Prize Lecture: The Role of Conformations in the Interplay of Structure and Dynamics in Macromolecular and Supramolecular Systems

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Summary: Following Paul J. Flory, the role of local chain conformation in determining the structure and dynamics of macromolecules is elucidated, employing advanced solid state NMR spectroscopy supported by X-ray scattering and dielectric spectroscopy. Topics covered include the local conformation in amorphous polymers, conformational memory, chain organization and dynamics in semicrystalline polymers, polypeptides, and rod-coil copolymers.

Keywords: dynamics; NMR spectroscopy; structure

Introduction

As pointed out by Paul J. Flory in his Nobel lecture[1] the configuration of a linear macromolecule in space involves enormous complexity. The number and variety of configurations (or conformations in the language of organic chemistry) that may be generated by execution of rotations about each of the skeletal bonds of a long chain, comprising thousands of bonds in a typical polymer, is prodigious beyond comprehension. To cope with this, he developed the Rotational Isomeric State (RIS) model, which allowed him to perform a quantitative statistical analysis of the chain conformation,[2] see also.[3] For a poly(ethylene) chain with perfect tetrahedral geometry, the different chain conformations can then be visualized on a diamond lattice. Along these lines, in our early work on studying molecular dynamics of solid polymers by ^{2}H-NMR[4] we used such a lattice model for analysis.[5] The local conformation of macromolecules can conveniently by probed by ^{13}C-NMR both in solution[6] and in the solid state.[7] It has pronounced effects on the chain organization and the molecular dynamics as will be shown below.

Conformation of Amorphous Polymers Probed by ^{13}C Solid State NMR

The basis of probing local conformation by NMR is the famous 'gamma-gauche effect', which says that the chemical shift of the central carbon in a vinyl polymer in an extended trans conformation is reduced by about 5 ppm for every γ-neighbour being in a *gauche* position.[6] In amorphous polymers, however, the dihedral angles may differ from perfect geometry. This became evident, when the local conformations in the solid state could directly be probed by high resolution magic angle spinning (MAS) ^{13}C-NMR,[7] combined with quantum chemical calculations of the chemical shift,[8] see Figure 1.

While the bands can roughly be assigned to specific local conformations as indicated, the individual spectral lines calculated after geometry optimization reveal a multitude of geometries with dihedral angles deviating for their 'ideal values'. It was highly

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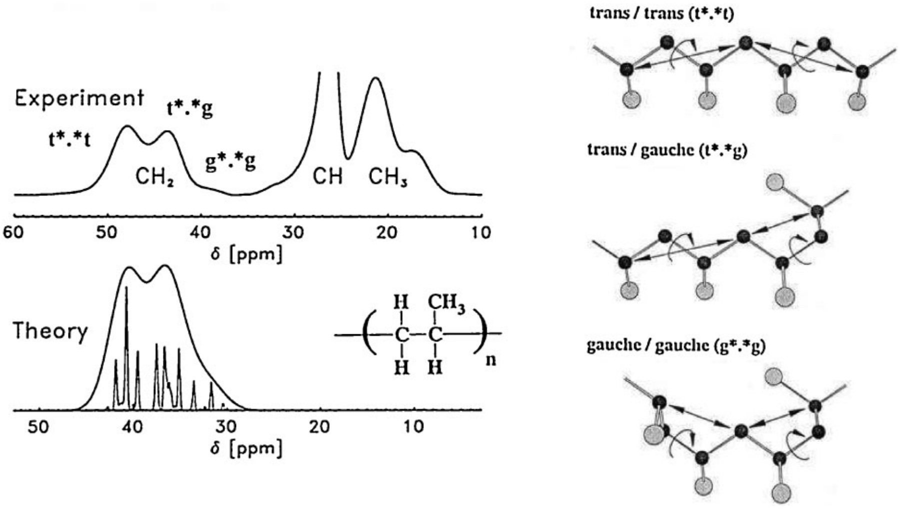

Figure 1.
Scheme of local conformations (right) and ^{13}C MAS NMR spectra of the CH_2 group in amorphous atactic poly(propylene).

impressive and gratifying, that in response to a corresponding question Flory told the author in private that he had been aware of such deviations from the start.

Conformational Memory

In simple polymers like atactic (propylene), the overall intensities of the bands correspond to the probabilities of the resspective conformations as calculated via the RIS description.[2] Stiff macromolecules with flexible side groups, however, lack conformational freedom within the backbone, which leads to formation of layered structures even in the melt and highly anisotropic motion.[9] The question then arises whether in more conventional polymers extended conformations involving several repeat units can exhibit conformational memory manifesting itself in collective anisotropic motions. Randomization of conformation leading to locally isotropic reorientation would then occur as a separated process on a longer time scale. Structurally heterogeneous poly(n-alkyl-methacrylates), which consist of a polar backbone and flexible nonpolar sidegroups R_n C_nH_{2n+1}, are candidates for polymers with such orientational memory, and indeed exhibit unusual relaxation behavior.[10] The backbone of these polymers containes extended syndiotactic sequences which leads to extended chain conformations, see Figure 2a.

Molecular dynamics of a macromolecular chain involves both conformational and rotational motions. Along these lines, the backbone dynamics of poly(n-alkyl methacrylates) has been clarified by advanced solid state NMR,[7] which enables us to probe conformational and rotational dynamics separately.[11] The former is encoded in the isotropic ^{13}C chemical shift as described above. The latter is probed via the anisotropic ^{13}C chemical shift of the carboxyl group with unique axis along the local chain direction. Randomization of conformations and isotropization of backbone orientation occur on the same timescale, yet they are both much slower than the slowest relaxation process identified previously by other methods.[10] This effect is attributed to extended backbone conformations, which retain conformational memory over many steps of restricted locally axial chain motion, Fig. 2b,c. These findings were rationalized in terms of a locally structured polymer melt, in which

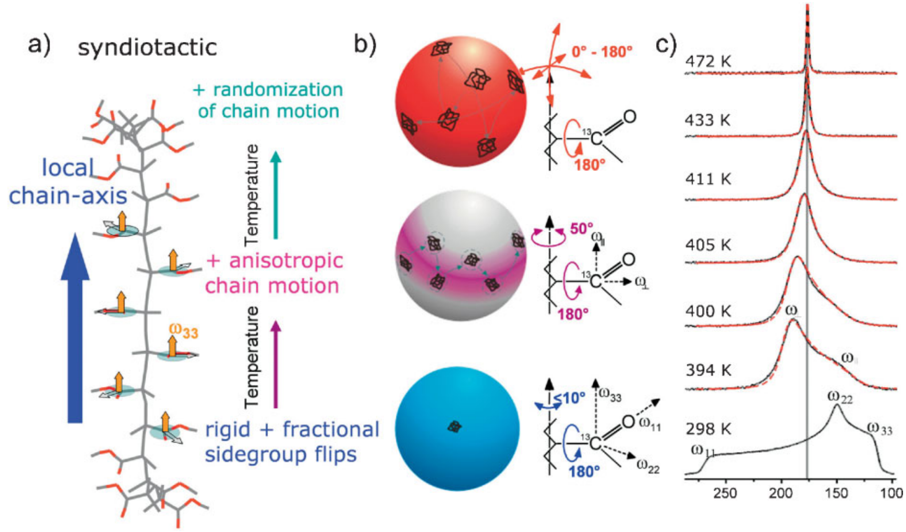

Figure 2.

a) Extended chain conformation of syndiotactic poly(n-alkyl methacrylates). b) anisotropc chain motion during glass process. c) ^{13}C NMR spectra indicating anisotropic motion above T_g as described in the text.

the polar and less flexible polymethacrylate backbones form disordered layers. This structure has been confirmed through temperature dependent wide-angle X-ray scattering (WAXS).[12] The anisotropic chain motion occurs within the layers, conformational randomization and rotational isotropization require extended chain units to translate from one structured unit to another. The variation in the molecular weight of PEMA showed that a minimum chain length of five to ten repeat units is required for this effect to occur.[13]

With this detailed understanding of the complex chain dynamics the peculiarities previously noted for the molecular dynamics in the series of poly(n-alkyl methacrylates)[10] are easily resolved. The WLF parameter describing the glass transition for the different members of the series deduced from the randomization/isotropization process exhibit minor systematic variations such as a decrease in fragility with alkyl side group length. Indeed, with increasing alkyl side group length, the structuring of the polymer melt is predominantly driven by side group association, the influence of the extended main chain conformations is reduced and the distinct relaxation and isotropization processes merge.[11]

Local Conformation and Chain Motion in Semicrystalline Polymers

Advanced solid state NMR techniques available today[14] provide new insight into one of the classics in polymer physics, namely the changes in mobility of chains in samples of different morphology.[15] In particular, the conformation of the chains at the interface between crystalline and non-crystalline regions in semi-crystalline polymers is crucial for their dynamics, see Figure 3. This was studied in ultrahigh molar mass linear poly(ethylene) in the solid state comparing the behavior of solution crystallized (SC) and melt crystallized (MC) samples.[16,17] As expected, the higher conformational order in the SC samples leads to a significantly reduced local mobility as probed via ^{1}H-^{13}C dipole-dipole couplings compared with the MC sample. In contrast, chain diffusion, where on a much longer time scale the all-trans

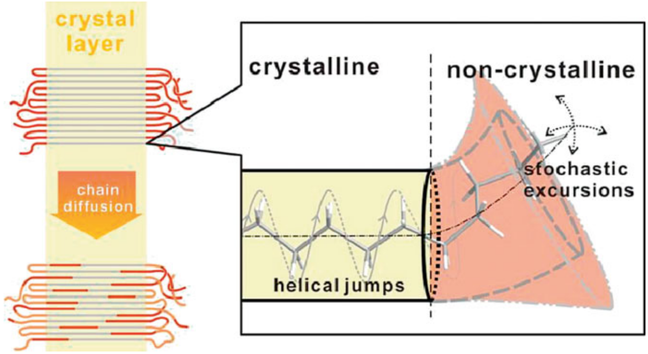

Figure 3.
Scheme of chain organization and chain motion in semi-crystalline polyethylene.

stems in the crystals diffuse to the gauche-containing non-crystalline regions and vice versa, is considerably faster in the SC samples. Thus, extended conformations in the interphase between crystalline and non-crystalline regions of SC samples apparently facilitate chain diffusion. The temperature dependence of the diffusive motion is alike in SC and MC samples. Therefore, the difference in time scale results from the entropy difference between SC and MC systems. Moreover, the diffusion constant of chain diffusion turns out to be largely independent of crystal thickness, which offers a new way to determine the length of all-trans stems in ultrahigh drawn fibres.[18]

The comparison of the diffusion constant for the chain diffusion and for the local motion in the crystallites, also available from NMR, is even more interesting. Substantial acceleration of the local mobility with increasing temperature, as compared to the chain diffusion, is observed, which can be attributed to the formation of defects in the expanded lattice. Contrary to textbook-knowledge,[15] however, these defects are not effective in moving the whole stem, despite the fact that their mobility is detected by mechanical relaxation. Instead, twist modes of the entire stem, as discussed by Mansfield and Boyd in 1978 already,[19] are apparently able to drive chain diffusion. Indeed, twists of the all-trans polymer chains have recently been detected in poly(ethylene) samples with equally spaced methyl braches by solid state NMR at ultrahigh magnetic fields.[20]

Local Conformations of Polypeptides

Local conformations also play a vital role in the organization of polypeptides (macromolecules composed of amino-acids): They are examples of molecules designed for use in drug delivery or gene therapy and thus have been the subject of intensive studies as reviewed recently.[21] Their two most common local conformations, known as secondary structures, are the α-helix, stabilized by intra-molecular hydrogen bonds, and the β-sheet, stabilized by inter-molecular H-bonds. These secondary structures can be probed directly by solid state NMR and their packing can be obtained by X-rays. In addition, the α-helical structure posts a permanent dipole moment along its backbone, and can, therefore, be used in dielectric spectroscopy (DS). For a review on applying a multiple-technique approach to elucidate structure and dynamics of polypetides see. ref.[22].

For example, *copolypeptides*, with their inherent nanometer length scale of phase separation, provide a means of manipulating both the type and persistence of peptide secondary structures. Based on the results from static (WAXS, SAXS) and dynamic

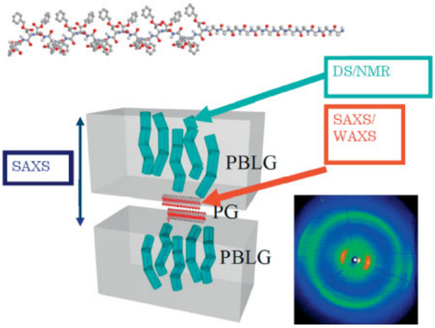

Figure 4.
Schematic model of PBLG-b-PG copolymers with fraction PBLG < 0.8 (i.e., within the lamellar nanodomain morphology) which is consistent with the results of the static (NMR, SAXS, WAXS) and dynamic (DS) methods.

(DS) methods, a schematic model is constructed in Figure 4 depicting the copolymer nanodomain and peptide secondary structures of a copolymer composed of poly(γ-benzyl-L-glutamate) (PBLG) and polyglycine (PG) inside the domains.[23] The two blocks are well separated, the PBLG helices are defected causing them to bend at certain positions (DS), PG chains fold several times (SAXS, WAXS) and finally PBLG α-helices and PG β-sheets (NMR) are organized perpendicular to the interface (WAXS). This reveals that the nanoscale confinement of dissimilar peptidic blocks can be used as a means of controlling the persistence length of the secondary peptide motifs with the larger effect produced for β-sheets. Issues that remain unexplored are the role of β-turns in folding of β-sheets, the associated kinetics and the role of the dimensionality of nanophases on the folding.

These effects should be taken into account when such peptides are considered for drug delivery. Polypeptide *star polymers* with a large hydrocarbon core were found to have several unanticipated properties.[24] First, with the aid of a polyphenylene core scaffold it was shown that there is a distinct change in the peptide secondary structure from coil/β-sheet conformations to α-helices accompanied by an abrupt increase in the hydrodynamic radii. This change in secondary structure and the consequences on the particles' diffusion, measured by confocal fluorescence correlation spectroscopy, can be crucial in the efficient design of multiple antigen peptides. Second, the bulk studies revealed a strong effect of the polyphenylene core on the peptide secondary motifs that could not be envisaged from their linear analogues. Clearly, the local conformation of the peptides is a key parameter for understanding these systems and the concerted use of the different techniques provides considerable more information than using either one alone.

Side Chain Conformation in Rigid-Rod Copolymers

In recent years the interest in polymer science has shifted considerably to include liquid crystals[25] and supramolecular structures.[26] In fact, lattice theory can be used to describe the order in liquids consisting of rodlike molecules polymers exhibiting nematic or cholesteric liquid crystallinity.[27] In the case of rigid rods, the axial ratio of the particles governs the concentration at which separation of a nematic or cholesteric phase sets in. For semi-rigid chains such as those of cellulose and its derivatives, the axial ratio of the Kuhn segment is the relevant parameter.

As a recent example, let us consider rod-coil copolymers such as oligo(p-benzamide)-poly(ethylene glycol) (OPBA-PEG) copolymers with an oligomeric rod and flexible PEG chains. They aggregate on a nanometer length scale, which is important for many applications like e.g. organic photovoltaics.[28] However, this aggregation behaviour and the driving forces such as hydrogen bonding and π-π interactions, as well as the role of the side groups, is not yet fully understood. These non-covalent interactions can be studied by advanced solid-state NMR, supported by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and polarization optical microscopy (POM).[29] As shown in

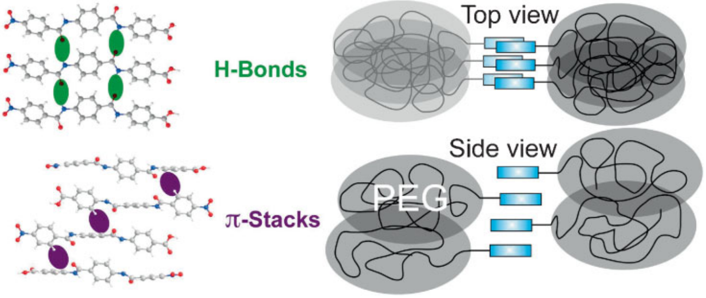

Figure 5.
Scheme packing of rod-coil copolymers. The rigid rods are held together by intermolecular hydrogen bonds and the space between the stacks is filled by the PEG side chains adopting a Gaussian coil like conformation.

Figure 5, longer OPBAs form layered ß-sheet like aggregates stabilized by amide hydrogen bonds, similar to polyamides with flexible side groups attached to the repeat units rather than the end groups.•[30] These aggregates are remarkably stable and apparently represent an equilibrium structure in both unsubstituted OPBAs and OPBA-PEG rod coil copolymers. The binding of the PEG also introduces a liquid-crystalline phase and the local structural order is improved in the copolymer, if the sample is preorganized in that phase. Thus, by combining different methods of structural investigation a model of local aggregation and packing in both the liquid-crystalline and the solid state could be developed.

Conclusion

Advances in synthesizing, characterizing, as well as understanding macromolecular and supramolecular systems led to an enormous variety and complexity in the field of polymer science,[31] yet chain conformation remains a central topic. The traditional separation in terms of structure vs. dynamics, crystalline vs. amorphous, or experiment vs. theory is increasingly overcome. As far as characterization of such materials is concerned, no experimental or theoretical/simulation approach alone can provide full information. Instead, a combination of techniques is called for and conclusions should be backed by results provided by as many complimentary methods as possible.[32] Combining scattering or NMR spectroscopy with computer simulation is well established today in the study of structure and dynamics of biomacromolecules but pioneering examples of such an approach in the supramolecular field involving the combination of spectroscopy and computer simulation have already been provided to elucidate the packing in columnar systems,[33] and the proton conducting network in a new type of proton conductor.[34] The development of NMR spectroscopy is far from complete. In particular, in order to meet the ever-increasing demands of miniaturization, the sensitivity of NMR spectroscopy has to be increased substantially and several approaches to respond to that challenge are underway.[35]

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[1] http://nobelprize.org/nobel_prizes/chemistry/laureates/1974/flory-lecture.pdf.
[2] P. J. Flory, "*Statistical Mechanics of Chain Molecules*", John Wiley, New York 1969.

[3] W. L. Mattice, U. W. Suter, *Conformational Theory of Large Moleculess*, Lylie-Interscience, New York 1994.

[4] H. W. Spiess, *Coll. Polym. Sci.* **1983**, *261*, 193.

[5] K. Rosenke, H. Sillescu, H. W. Spiess, *Polymer* **1980**, *21*, 757.

[6] A. Tonelli, ''*NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*'', VCH, Weinheim 1989.

[7] K. Schmidt-Rohr, H. W. Spiess, ''*Multidimensional Solid-State NMR and Polymers*'', Academic Press, New York 1994.

[8] R. Born, H. W. Spiess, *Macromolecules* **1995**, *28*, 7785.

[9] M. Mierzwa, G. Floudas, M. Neidhöfer, R. Graf, H. W. Spiess, W. H. Meyer, G. Wegner, *J. Chem. Phys.* **2002**, *117*, 6289.

[10] M. Beiner, *Macromol. Rapid Commun.* **2001**, *22*, 869–895.

[11] M. Wind, R. Graf, A. Heuer, H. W. Spiess, *Phys. Rev. Lett.* **2003**, *91*, 155702.

[12] M. Wind, R. Graf, S. Renker, H. W. Spiess, W. Steffen, *J. Chem. Phys.* **2005**, *122*, 014906.

[13] M. Wind, R. Graf, S. Renker, H. W. Spiess, *Macromol. Chem. Phys.* **2005**, *206*, 142.

[14] H. W. Spiess, *J. Polym. Sci. A - Polymer Chemistry* **2004**, *42*, 5031.

[15] G. Strobl, *The Physics of Polymers*, Springer-Verlag, Berlin 1997.

[16] Y.-F. Yao, R. Graf, H. W. Spiess, S. Rastogi, D. R. Lippits, *Phys. Rev. E*, **2007**, *76*, 060801(R).

[17] Y.-F. Yao, R. Graf, H. W. Spiess, S. Rastogi, *Macromolecules* **2008**, *41*, 2514–2519.

[18] Y.-F. Yao, R. Graf, H. W. Spiess, S. Rastogi, *Macromol. Rapid Commun.* **2009**, *30*, 1123.

[19] M. Mansfield, R. H. Boyd, *J. Polym. Sci. B - Polymer Physics* **1978**, *16*, 1227.

[20] Y. Wei, R. Graf, J. C. Sworen, C.-Y. Cheng, C. R. Bowers, K. B. Wagener, H. W. Spiess, *Angew. Chem. Int. Ed.* **2009**, *48*, 4617.

[21] H. A. Klok, *Macromolecules* **2009**, *42*, 7990.

[22] G. Floudas, H. W. Spiess, *Macromol. Rapid Commun.* **2009**, *30*, 278.

[23] P. Papadopoulos, G. Floudas, I. Schnell, T. Aliferis, H. Iatrou, N. Hadjichristidis, *Biomacromolecules* **2005**, *6*, 2352.

[24] K. Koynov, G. Mihov, M. Mondeshki, C. Moon, H. W. Spiess, K. Müllen, H.-J. Butt, G. Floudas, *Biomacromolecules* **2007**, *8*, 1745.

[25] *Handbook of Liquid Crystals*, D. Demus, J. Goodby, G. W., Gray, H. W., Spiess, V. Vill, Eds., Wiley-VCH, Weinheim 1998.

[26] J. M. Lehn, *Science* **2002**, *295*, 2400.

[27] P. J. Flory, *Adv. Polym. Sci.* **1984**, *59*, 1.

[28] J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718.

[29] A. Bohle, G. Brunklaus, M. R. Hansen, T. W. Schleuss, A. F. M. Kilbinger, J. Seltmann, H. W. Spiess, *Macromolecules* **2010**, *43*, 4978–4985.

[30] A. Adam, H. W. Spiess, *Macromol. Chem., Rapid Commun.* **1990**, *11*, 249.

[31] C. K. Ober, S. Z. D. Cheng, P. T. Hammond, M. Muthukumar, E. Reichmanis, K. L. Woolex, T. P. Lodge, *Macromolecules* **2009**, *42*, 465.

[32] H. W. Spiess, *Macromolecules* **2010**, *43*, 5479.

[33] C. Ochsenfeld, S. P. Brown, I. Schnell, J. Gauss, H. W. Spiess, *J. Am. Chem. Soc.* **2001**, *123*, 2597.

[34] Y. L. Lee, T. Murakhtina, D. Sebastiani, H. W. Spiess, *J. Am. Chem. Soc.* **2007**, *129*, 12406.

[35] H. W. Spiess, *Angew. Chem. Int. Ed.* **2008**, *47*, 639.