

ARRANGEMENT AND DYNAMICS OF MOLECULAR SEGMENTS AS SEEN BY DIPOLAR SOLID-STATE NMR

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Measurements of dipolar couplings generally yield direct information on internuclear distances. The requirement of labeled materials, however, renders application of standard solid-state ^{13}C - ^{13}C (^{15}N) correlation techniques impractical for solving of many academic and industrial problems. In many cases the synthetic effort necessary to prepare selectively and/or uniformly labeled molecular systems is really daunting. The only way how to overcome this limitation is measurement of dipolar couplings involving ^1H atoms (e.g. ^1H - ^1H , ^{13}C - ^1H etc). Recent methodological advances in developments of homodecoupling sequences (FSLG, PMLG, DUMBO, e-DUMBO etc.) improved sensitivity and resolution in ^1H frequency dimension in such way that the basic concept of correlation experiments could be applied on systems at natural isotopic abundance. Subsequent analysis of the obtained highly-resolved correlation patterns provides sufficient number of dipolar contacts and distance restraints that can be used to reconstruct basic structural motifs and fragments not only for highly organized and well arranged crystals of organic solids but also for partially ordered polymer systems. Several examples of utilizations of heteronuclear correlation experiments and their analysis will be demonstrated and discussed. However, dipolar couplings provide information not only about interatomic distances. From the motional averaging of dipolar couplings valuable information about segmental dynamics – motional amplitudes – can be derived. Recently developed pulse sequences designed for the “domain-selective” recoupling of heteronuclear dipolar interactions in mobile amorphous and/or rigid crystalline phases [1] have been successfully applied to describe amplitudes of segmental motions in heterogeneous polymer nanocomposites below and above glass-transition temperature [2,3]. It will be also demonstrated that the applied dipolar recoupling experiments yield valuable data that can be related to the mechanical and thermomechanical properties of polymer nanocomposites. Finally, the analysis of segmental dynamics in crystalline active pharmaceutical ingredients (API) will be discussed with respect to the crystal disorder and to the thermodynamic stability of various polymorphs.

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References

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