Chapter 2

Developments in Solid-State NMR Spectroscopy of Polymer Systems

Antonio Martínez-Richa and Regan L. Silvestri

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.70116

Abstract

Solid-state nuclear magnetic resonance (NMR) has long emerged as a valuable technique for characterizing the molecular structure, conformation, and dynamics of polymer chains in various polymer systems. The principles of the solid-state ^{13}C NMR cross-polarization experiment are described along with corresponding relaxation measurements. The ensuing recent applications of these techniques to different polymer systems are reviewed, with selected examples that have appeared in the recent literature. All of these applications of solid-state NMR to polymers have one feature in common: the interpretation of spectroscopic observations as related to the structural features and physical properties of the polymer.

Keywords: polymers, solid-state NMR, structure-property relationship, polymer morphology, polymer dynamics, NMR relaxation time

1. Introduction

Solid-state nuclear magnetic resonance (NMR) spectroscopy is at this time well-established as a valuable technique for characterizing a variety of polymer systems. A multitude of NMR experiments can be used to gain valuable practical information about the molecular structure, conformation, and dynamics of polymer chains in various polymer systems. Such information is useful in the design of polymer properties, and therefore the technique of solid-state NMR has been widely applied to numerous polymer systems.

The use of solid-state ^{13}C NMR is well established for elucidation of cross-linking structures in elastomers and bonding structures in adhesives [1], and the technique continues to be applied

to new elastomer and adhesive systems. These same techniques are now being applied to new polymer systems such as self-assembled polymers, advanced functional polymers, electro-conducting polymers, microporous materials, and proteins [2].

2. High-resolution ^{13}C NMR spectroscopy of solid polymers

Nuclei with a spin quantum number of $I = ½$ such as ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{15}N, and ^{31}P yield high-resolution NMR spectra and are therefore particularly informative in the study of polymer systems. These nuclei display spectra with unique peaks for each magnetically inequivalent nuclei in the chemical structure, essentially enabling the study of individual atomic positions within the chemical structure of a polymer [3]. As such, localized information can be ascertained about individual atomic sites within the chemical structure of a polymer.

In solution, local magnetic fields experienced by nuclei are averaged by rapid isotropic motions resulting in the observation of relatively sharp NMR peaks. Polymers however are largely used not in the solution state but as structural engineered materials such as plastics and elastomers in the solid state. Therefore, there is a need to study them as solids, to characterize their properties in the solid state, which is the state that they will be used as structural materials. Observation of the ^{13}C nucleus in the solid state is complicated by line broadening caused by strong dipolar interactions with the abundant ^{1}H isotope. This line broadening is reduced by heteronuclear dipolar decoupling (DD), a high powered radio frequency (rf) pulse at the ^{1}H frequency during the time in which the ^{13}C signal is observed [4].

The collection of solid-state NMR spectra is also complicated by high chemical shift anisotropy, which is motionally averaged in the liquid state. The line broadening caused by chemical shift anisotropy in the solid state is reduced by a technique termed magic angle spinning (MAS). The broad chemical shift anisotropy pattern of a solid is reduced to a single peak at the isotropic chemical shift by spinning the solid sample, typically at a rate of a few thousand hertz, at an angle of precisely 54.74° relative to the static magnetic field [5].

The ^{13}C isotope being only 1.1% naturally abundant, and the heteronuclear dipolar coupling and chemical shift anisotropy of solids being only partially reduced by DD and MAS, respectively, results in an inherently low signal-to-noise ratio for solid-state spectra. The ^{13}C signal for solid samples is enhanced by a technique termed cross-polarization (CP). Cross-polarization is achieved by simultaneously applying spin locking rf pulses to both ^{13}C and ^{1}H nuclei. The spin locking rf pulses are adjusted to reach a state where both nuclei process at the same frequency, a special condition referred to as the Hartmann-Hahn match. Under these conditions, magnetization is transferred from the naturally abundant ^{1}H spin reservoir to the more dilute ^{13}C spin reservoir, resulting in signal enhancement of the ^{13}C spin reservoir. As a result, an enhanced ^{13}C signal can be observed for solid samples [6].

The combination of these three techniques (DD, MAS, and CP) into one experiment provides a method for the collection of high-resolution ^{13}C NMR spectra of solids. The results observed by applying these techniques, in combination progressively and ultimately, simultaneously in one experiment, are shown in **Figure 1** [7]. The method of simultaneously combining DD,

MAS, and CP has become routine for solid samples, and applications to polymer systems are sufficiently plentiful to fill entire professional reference textbooks [8]. Particularly, application of the solid-state NMR technique has historically proven to be highly informative in elucidation on the conformational structure of solid polymers via chemical shift analysis and determination of cross-linking structures of cross-linked solid polymers.

Beyond the DD, MAS, and CP experiment to collect high-resolution solid-state spectra, sophisticated and elegant rf pulse sequences are now used to perturb the magnetization in specific ways. As such, observation of the magnetization as it processes back to equilibrium via various cleaver rf pulse sequences allows the collection of information far beyond the simple spectrum.

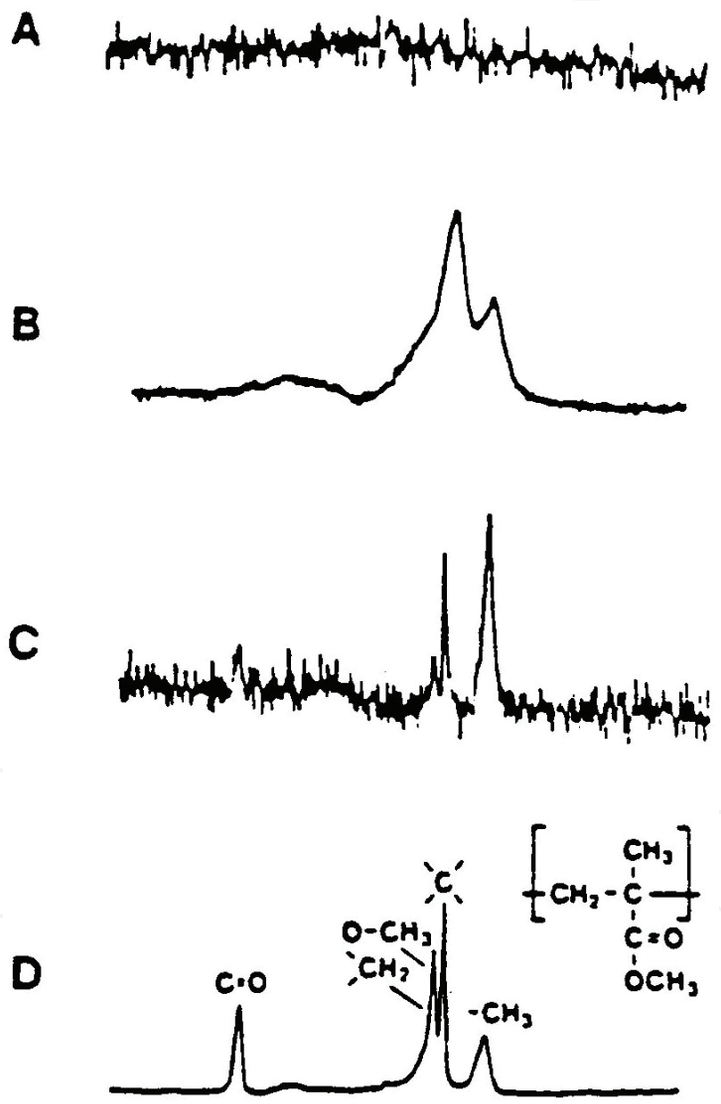

Figure 1. The ^{13}C NMR spectra of poly(methyl methacrylate) in the solid state under various experimental conditions: (a) using the experimental conditions for solution spectra, no discernible peaks are observed for the solid sample; (b) using dipolar decoupling with cross-polarization permits the observation of broad chemical shift anisotropy patterns; (c) using dipolar decoupling with magic angle spinning reduces the broad chemical shift anisotropy patterns to resolvable peaks; and (d) the combination of all three techniques, dipolar decoupling with magic angle spinning and cross-polarization, facilitates the observation of a high-resolution spectrum for the solid sample. Reprinted from Ref. [7].

For example, the study of selectively pulsed magnetization as it relaxes back to equilibrium yields insight into not only the molecular structure, but also the molecular dynamics of a polymer system. Relaxation of a nucleus back to equilibrium is modulated by fluctuations in the local magnetic field which the nucleus experiences, and the local field is modulated due to the local environment, including not only the physical-chemical structure around a nucleus, but also molecular motion that the nucleus is involved in. Various pulse sequences allow the measurement of relaxation parameters including T_1, T_2, and $T_{1\rho}$, which yield information about molecular motions in different frequency ranges, which occur over different scales of distance [9]. Beyond the direct measurement of these relaxation parameters, other pulse sequences exploit these relaxation phenomena to yield data which can be interpreted in terms of polymer structure and properties.

Two-dimensional (2D) NMR techniques enhance the resolution of a traditional one-dimensional spectrum by spreading the peaks out in a second dimension. Two-dimensional NMR techniques also facilitate the observation of through bond or through space interactions, where through space interactions being particularly related to the physical structure of polymers such as conformation [10]. While 2D NMR techniques are routine for solutions, they are still considered by some to be experimentally cumbersome in the solid state. Nonetheless, there has been considerable progress recently in the development of experimentally practical pulse sequences for 2D NMR of solid samples [11].

3. Applications to various polymer systems

3.1. Carbohydrates

Wood is a complex heterogeneous material composed mainly of hemicellulose, cellulose, and lignin. Solid-state NMR spectroscopy can discriminate wood samples based upon their provenance. In that regard, the traceability of wood samples can be undertaken by analyzing the solid-state NMR peak patterns in their MAS and CP-MAS spectra.

This technique has been used to characterize the chemical composition of wood, and the effects of aging, decomposition, and some physical or chemical treatments on the polymer structure. Recently, this technique was used to analyze maple samples from Norway [12] and spruce samples from Finland, Poland, and Italy [13]. The chemical structures of various components in soft wood are shown in **Figure 2**. Carbon-13 CP-MAS NMR spectra for spruce wood from Finland, Poland, and Italy are shown in **Figure 3** with resonance peaks labeled to correspond with the structures shown in **Figure 2**. While the same peak pattern is present in all three samples, small differences (mainly in peak intensity) can be distinguished between the three spectra.

In the spectral region 110–160 ppm, differences in the lignin aromatic components can be distinguished, whereas in the spectral region from 15 to 110 ppm, differences in the signals for cellulose and hemicellulose can be observed. In that regard, the most intense peaks in the spectra 12 and 13 are due to the C-2, C-3, and C-5 carbons of the carbohydrates. The two peaks 10 and 11 are assigned to C-4, in crystalline and amorphous (or less ordered surface) cellulose,

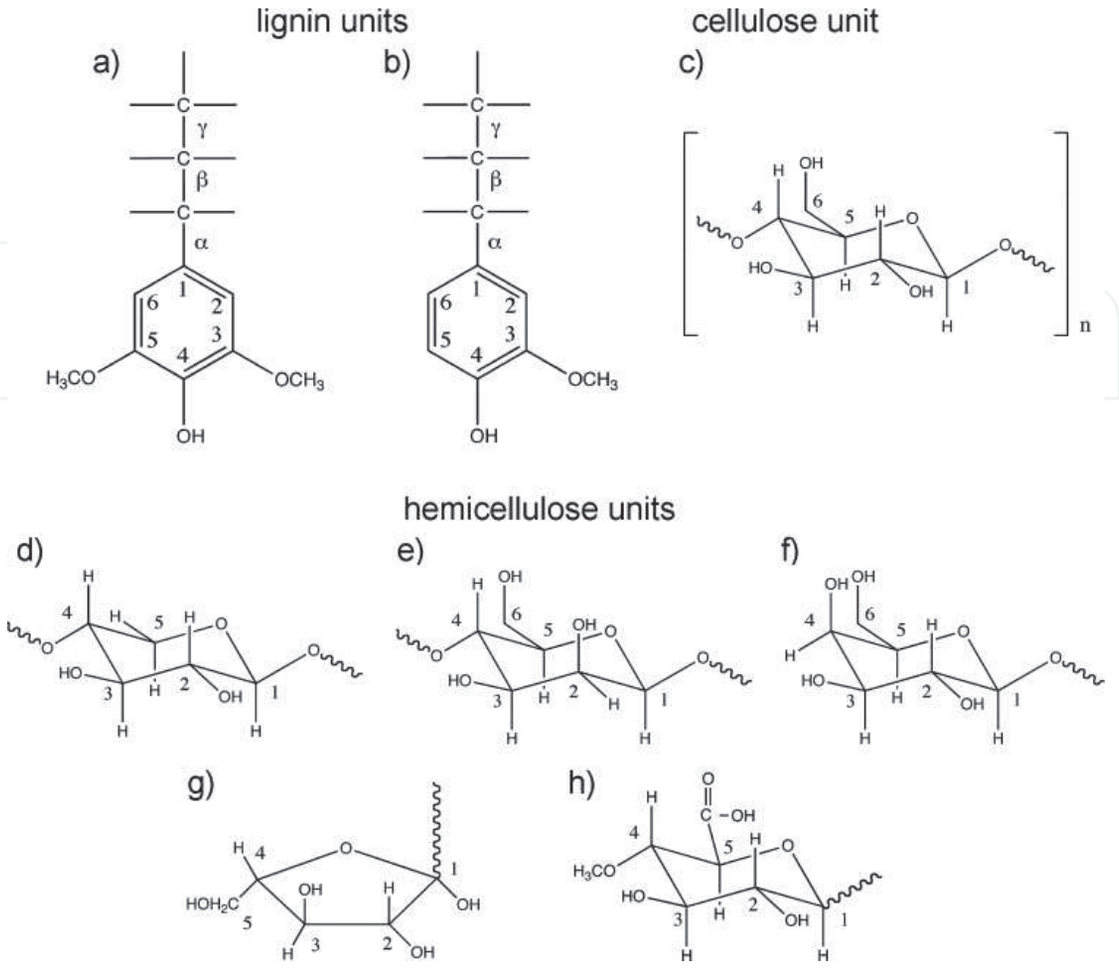

Figure 2. Chemical structures of various wood components in softwood. The numbering scheme corresponds to the resonance peaks as labeled in **Figure 3**. Reprinted from Ref. [13].

respectively. Peak 15 is related to C-6 in cellulose and Cγ in lignin. Peak 8 represents the C-1 of cellulose, with a high-field shoulder 9 attributed to hemicellulose (102 ppm). Only two signals can be undoubtedly attributed to hemicellulose: the methyl carbon peak 18 and the carboxylic carbon peak 1; both of these are rather weak in intensity. Three groups of signals in the range 160–105 ppm are attributed to the three aromatic units constituting the lignin lattice. Finally, the small peak 16 is assigned to the lignin methoxyl group.

As differences in peak pattern intensities for the three samples are small, $^{1}H\ T_{1\rho}$ measurements were obtained using a variable CP contact time experiment. The results suggest that higher polymer mobility and a higher homogeneity are observed in spruce wood from Finland, relative to a lower homogeneity measured in samples from both Italy and Poland.

3.2. Protein systems

Solid-state NMR spectroscopy has been widely applied to study a variety of protein systems. Various modern solid-state NMR techniques can be applied to gain insights into biophysics and structural biology in proteins.

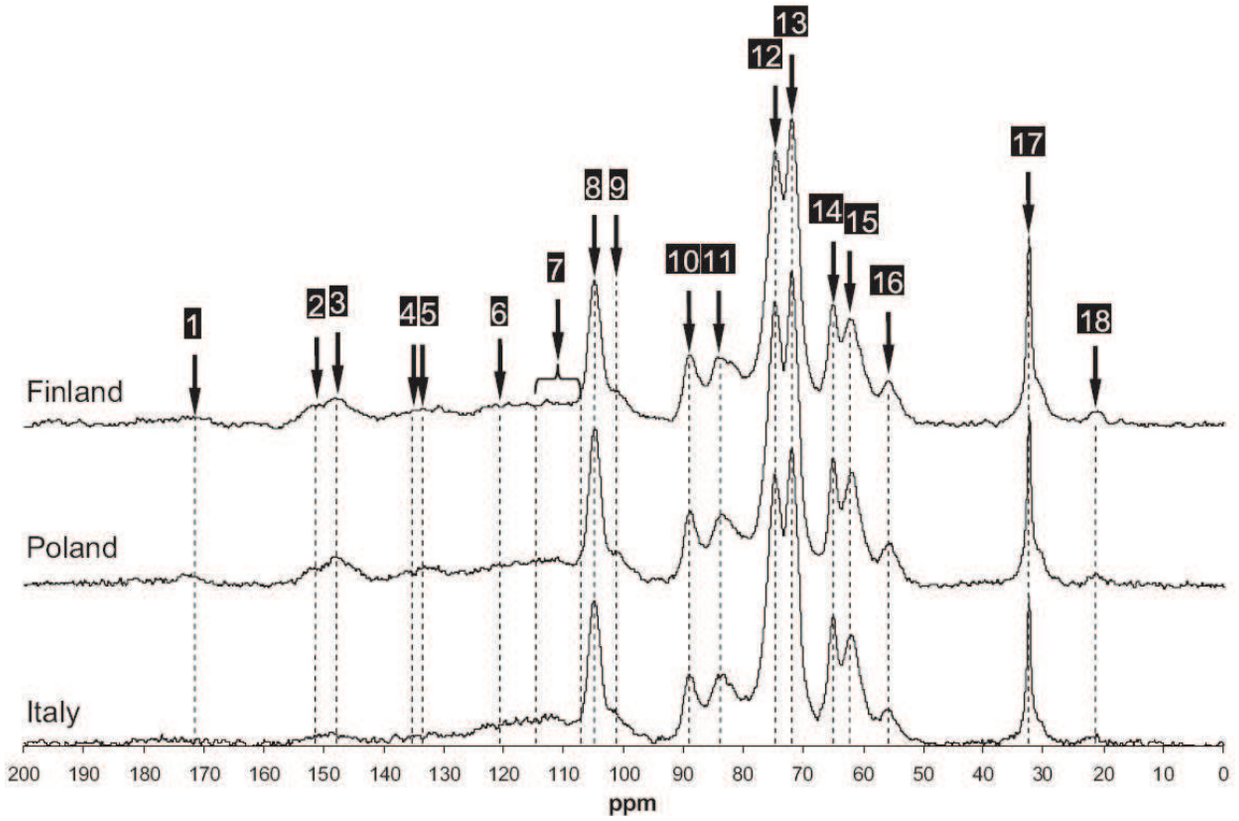

Figure 3. Solid-state ^{13}C NMR spectra of spruce woods differing in provenance and their peaks assignments. Differences in peak intensities can be used to distinguish between the geographic origins of woods. Reprinted from Ref. [13].

Peptide nanoassemblies have been studied by solid-state NMR. Using the recent development of high-field MAS dynamic nuclear polarization (MAS-DNP), an increase in sensitivity for the peaks of crystalline components of the polymer system can be achieved [14]. Using this approach, self-assembled structures of systems based on diphenylalanine dipeptide (FF) have been studied. These proteins have applications as organic semiconductors, and have been reported as a core motif of Alzheimer's amyloid-β. Supramolecular structural information such as hydrogen bonding and π-π stacking can be improved using dynamic nuclear polarization. Ultimately, an increase in sensitivity by an overall factor of 320 is achieved by using DNP.

Self-assembly peptide nanostructure can be studied by solid-state NMR. MAX8 is an amphiphilic peptide composed of 20 amino acids, having the amino acid sequence VKVKVKVKVDPPTKVEVKVKVNH2, where K and E are hydrophilic residues and V hydrophobic residues [15]. The self-assembled peptide contains a β-strand hairpin structure aligned into antiparallel β-sheets. As is commonly observed, changes in supramolecular structure can be induced by changes in temperature, pH, and ionic strength. The CP-MAS spectra of labeled and unlabeled MAX8 nanofibers are shown in **Figure 4**. The observed chemical shifts for the amino acid residues 1–8 and 13–20 indicates that they form part of a β-hairpin conformation. Polymorphism of K residues occurs uniformly across the MAX8 amino acid system. Calculations of ϕ and φ backbone torsion angles, derived from peak positions using commercial software, were consistent with β-strand secondary structures for residues 1–8 and

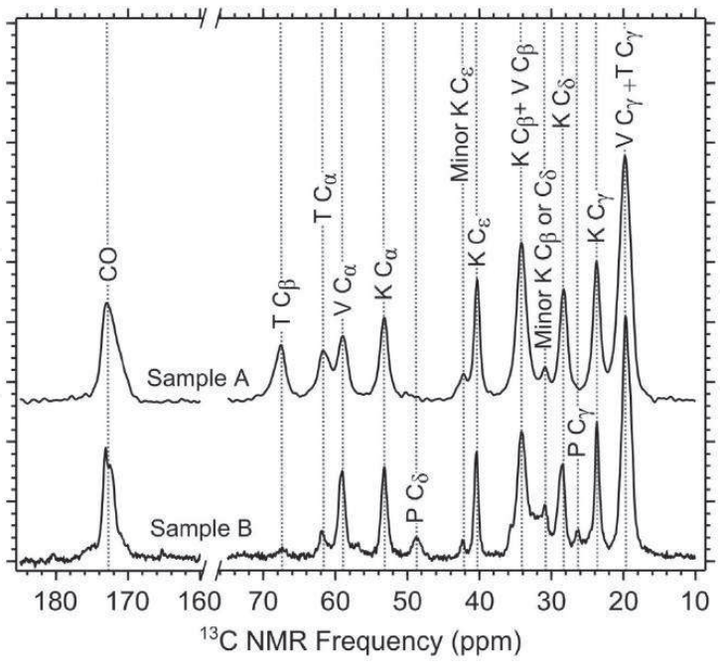

Figure 4. Solid-state ^{13}C CP-MAS spectra of labeled and unlabeled MAX8 nanofiber, a peptide composed of 20 amino acids. Observed chemical shifts for the amino acid residues allow determination of the three dimensional conformational structure of the peptide. Reprinted from Ref. [15].

13–20. Further evidence of the existence of a close β-hairpin conformation was obtained by (a) the analysis of cross-peaks in a 2D DARR $^{13}C—^{13}C$ NMR experiment, and (b) $^{13}C—^{13}C$ dipolar recoupling NMR experiments using the PITHIRDS-CT technique. The PITHIRDS-CT technique is a constant-time dipolar recoupling sequence in solid-state NMR with MAS, which yields experimental data that is insensitive to rf pulse imperfections and nuclear spin relaxation processes. This sequence has been widely used to determine intermolecular distances and molecular conformations in solid ^{13}C and ^{15}N labeled compounds, and as such one of the most important applications of this technique has been the study of biological samples such as amino acids and amyloid fibrils.

In a similar approach, β-sheet nanocrystalline domains in phosphorylated serine-rich motifs in caddisfly larval silk were studied by ^{13}C and ^{31}P solid-state NMR [16]. ^{13}C NMR data from isotopically enriched caddisfly silk, packed in its natural hydrated environment, are shown in **Figure 5**. ^{13}C chemical shifts were identified using $^{13}C—^{13}C$ DARR and $^{1}H \rightarrow {}^{31}P \rightarrow {}^{13}C$ DCP NMR experiments. Differences between CP-MAS and DD-MAS spectra are due to the aqueous environment. Water-solvated residues with a short T_1 exhibit enhanced signals in the DD-MAS spectrum, whereas carbons located in more rigid environments are better observed in the CP-MAS spectrum. An enhanced peak for the unmodified serine β carbon is seen in the DD-MAS spectrum, suggesting higher mobility. On the other hand, the signal of the phosphorylated serine β carbon is broader, indicating that these moieties mainly reside in the β-sheet regions. Similar conclusions have been derived for Valine residues. However, glycine and leucine residues, often seen in GGX repeats, exist predominantly in a random or disordered conformation.

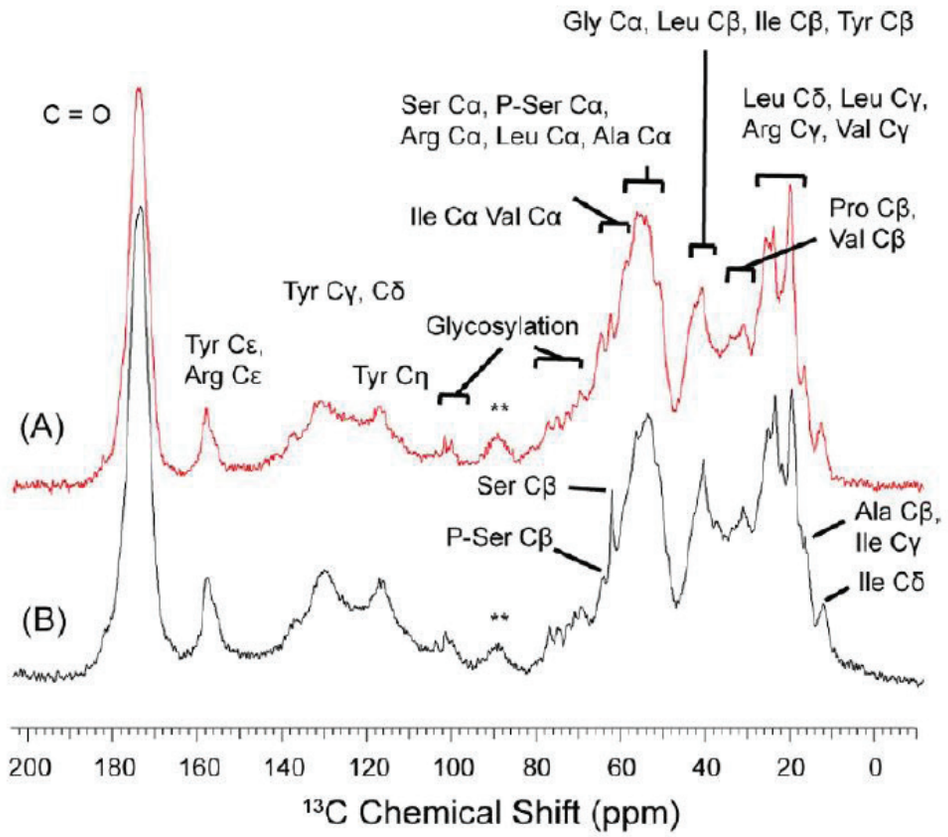

Figure 5. Solid-state ^{13}C NMR of isotopically enriched caddisfly silk from the species *Hyllisia consimilis* in its natural water-hydrated environment. (A) $^{1}H \rightarrow {}^{13}C$ CP-MAS NMR, and (B) ^{13}C DD-MAS NMR using a fast (1 s) repetition time. Peaks, which have a higher intensity without cross-polarization are in more mobile water-solvated regions, whereas peaks which have a higher intensity with cross-polarization are in more rigid environments in the β-sheet regions. Carbonyl spinning side bands are marked with a double asterisks. Reprinted from Ref. [16].

3.3. Conducting polymers

Advances in conducting and semiconducting materials have led to enhancements in the performance of organic thin transistors, organic photovoltaics, and other devices. High molar mass poly(3-hexylthiophene) (P3HT), an organic semiconductor, has been studied by solid-state ^{13}C CP-MAS NMR. Information at the subnanometer length scale can be obtained via solid-state NMR.

Recently, a modified approach to this technique has facilitated a correlation between peak pattern observed in CP-MAS spectra and the degree of crystallinity [17]. Measurements of order in semicrystalline, high molar mass poly(3-hexylthiophene) (P3HT) were made via solid-state ^{13}C CP-MAS. The relative degrees of order were compared between two films under different drying conditions: one slow-dried and one fast-dried. Ordered and disordered fractions within the polymer were separated using a $T_{1\rho}$ filtered CP-MAS experiment. The spectrum for the ordered P3HT component is then obtained by spectral subtraction, as shown in **Figure 6**. The peak pattern of the crystalline component for slow-dried P3HT is narrower than that observed for the fast-dried sample. NMR does not measure long-range order, but instead is sensitive to order on a subnanometer scale. Line shape analysis shows that chains in noncrystalline regions

http://dx.doi.org/10.5772/intechopen.70116

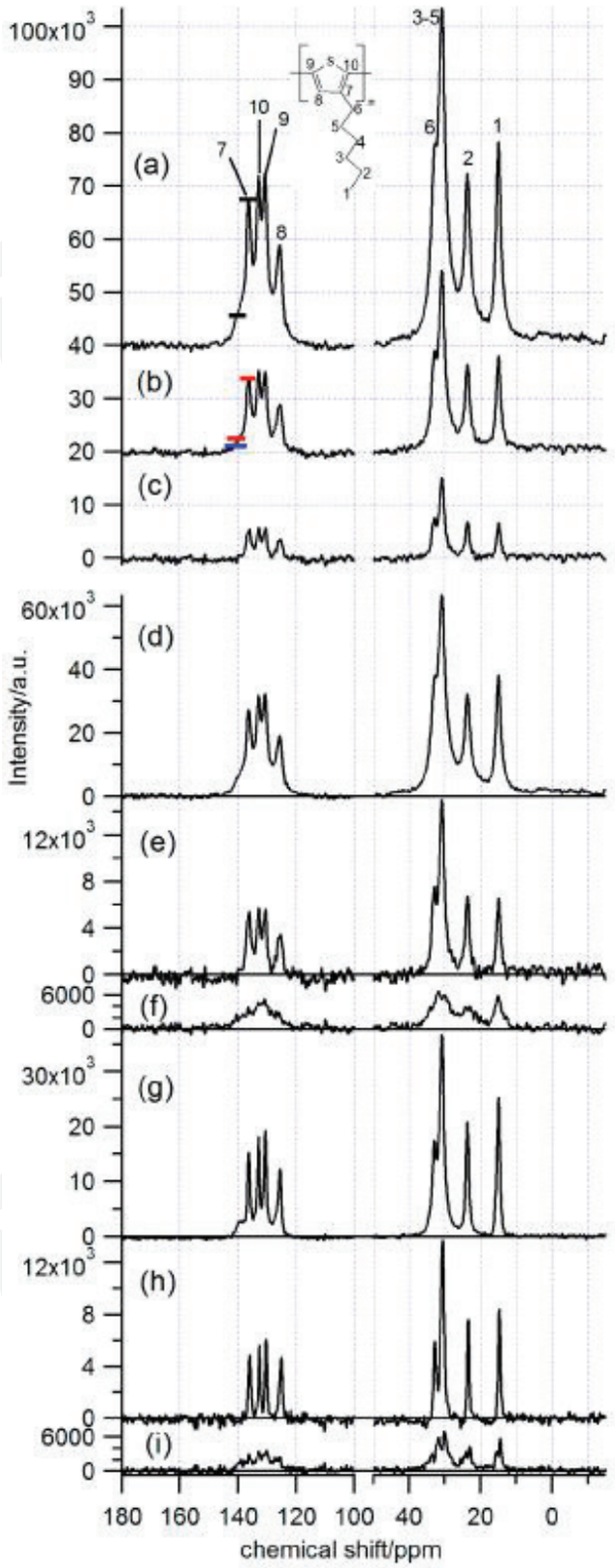

Figure 6. Solid-state ^{13}C CP-MAS spectra of the fast-dried organic semiconductor poly(3-hexylthiophene) (P3HT) (a) without and (b) with a $T_{1\rho H}$ spectral editing (spin-lock) pulse prior to cross-polarization, as well as the difference spectrum: (c) = (b) – (0.35 × (a)). The (d) CP-MAS spectrum for fast-dried P3HT, and (e) its ordered and (f) disordered fractions. The (g) CP-MAS spectrum for slow-dried P3HT, and (h) its ordered and (i) disordered fractions. Reprinted from Ref. [17].

can exhibit uniform local packing, which is presumed to be the result of uniform molecular conformations. Ultimately, observation of a narrower peak pattern of the crystalline component for slow-dried than for fast-dried is interpreted to mean that the quality of order is different, and that P3HT may be classified as a conformationally disordered crystal.

The solid-state NMR technique provides information about the conducting polymer system, which is close to the natural state and natural local conformation and packing arrangement. As such, information from solid-state NMR experiments may be regarded as favored to information derived by other techniques such as wide-angle X-ray scattering and differential scanning calorimetry.

4. NMR relaxation

The magnetic properties of a nucleus are modulated by the magnetic fields of neighboring nuclei. As molecular motions occur in the local environment changes resulting in altered interactions between nuclear spins. The study of NMR relaxation parameters yields information about the molecular motions in polymer systems.

The NMR relaxation parameters, which are most commonly measured are T_1, T_2, and $T_{1\rho}$. T_1 is the so-called spin-lattice relaxation time, T_2 is the spin-spin relaxation time, and $T_{1\rho}$ is the spin-lattice relaxation time in the rotating frame. These various relaxation parameters are related to molecular motions on varied time scales, and the correlation time of a molecular motion is related to the scale or distance over which a molecular motion occurs. As such, each of the relaxation parameters T_1, T_2, and $T_{1\rho}$ is characteristic of molecular motions involving different frequency ranges, which occur accordingly over different distance scales as shown in **Figure 7**. The relaxation parameter T_1 probes fast motions with frequencies in the MHz regime; such fast motions are small-scale short-range motions, which are typically internal to a molecule. The relaxation parameter $T_{1\rho}$ probes slower motions with frequencies in the kHz regime; these relatively slower motions occur over a larger distance and correspond to long chain motions in polymers. The theoretical relationship between the ^{13}C NMR relaxation parameters T_1, T_2, and $T_{1\rho}$ in the solid state and correlation time τ_c are shown in **Figure 8** [18].

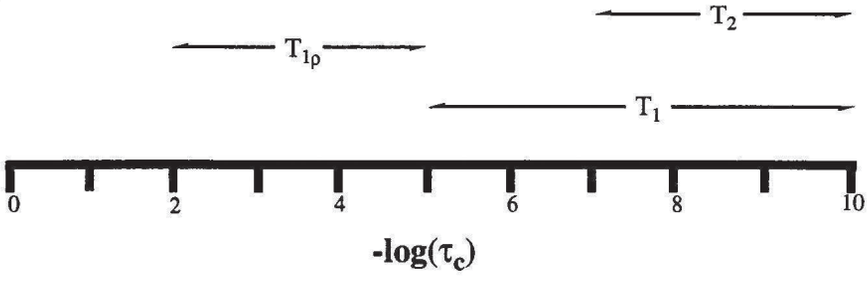

Figure 7. The solid-state ^{13}C NMR relaxation parameters T_1, T_2, and $T_{1\rho}$ (in seconds) and the corresponding correlation times τ_c (in seconds) for the motions which they are sensitive to. Each of the relaxation parameters T_1, T_2, and $T_{1\rho}$ are characteristic of molecular motions in different frequency ranges which occur over different distance scales.

http://dx.doi.org/10.5772/intechopen.70116

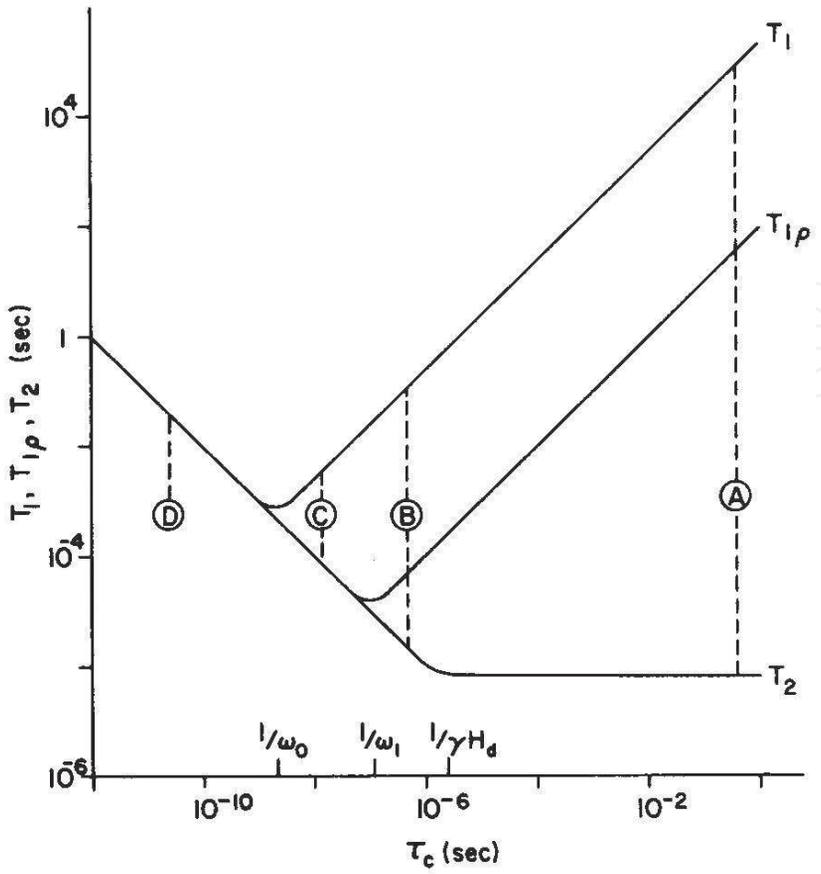

Figure 8. Theoretical dependence of the relaxation times T_1, T_2, and $T_{1\varrho}$ on the correlation time τ_c of the molecular motions responsible for the relaxation, as predicted by molecular motions that result in changes in dipole-dipole interactions. Region A is characteristic of a rigid lattice, region B of a nonrigid solid, region C of a viscous liquid, and region D of a nonviscous liquid. Reprinted from Ref. [18].

Semi-crystalline polymers are composed of amorphous (noncrystalline) bulk material, which contains crystalline domains. As NMR relaxation is modulated not only by physical-chemical structure, but also by molecular motions, the study of NMR relaxation yield insight into phases and phase structure in such multiphase polymer systems. The different domains present in such polymer materials display differences in molecular mobility, with the motion in crystalline domains being more restricted. Nuclei in amorphous domains show a higher mobility than those of nuclei in more rigid crystalline domains. Insight into polymer phase structure can be gained by the measurement of the NMR relaxation parameters T_1, T_2, and $T_{1\varrho}$ [19].

There are numerous examples of how such NMR relaxation studies have been exploited to yield valuable information about the phase structure in polymer blends. In the interest of blending thermoplastics with biodegradable polymers, the degree of crystallinity of microbial poly(ε-L-lysine) has been estimated via ^{13}C T_1 relaxation experiments [20]. In another study, the domain size of poly(ε-L-lysine) blended with poly(vinyl isobutyl ether) was estimated via ^1H spin-lattice relaxation experiments, and further miscibility of blends prepared under various processing conditions was explained in terms of crystallinity observations from the relaxation experiments [21]. In a similar study, phase separation in starch/polycaprolactone blends was investigated and the length scale over which phase separation occurs was determined via ^{13}C T_1, ^1H T_1, and ^1H $T_{1\varrho}$

relaxation experiments [22]. Further, the effect of the concentration of poly(ethylene glycol) in poly(ethylene glycol)/silica blends has been investigated via ^{13}C T_1 and ^{1}H $T_{1\varrho}$ relaxation experiments yield information about inhomogeneous separated phases [23]. As a final example, blends of poly(ethylene terephthalate) toughened by natural rubber have been studied by ^{13}C chemical shift and ^{1}H $T_{1\varrho}$ relaxation experiments, yielding evidence of interactions between the carbonyl groups of the poly(ethylene terephthalate) with some functionality in the natural rubber [24].

Likewise, there are numerous examples of how such NMR relaxation studies have been exploited to yield practical and useful information about copolymer systems. For example, poly(styrene-butadiene-styrene) has been found to compatibilize otherwise incompatible blends of polystyrene/polybutadiene, and ^{1}H T_1, ^{1}H T_2 and ^{1}H $T_{1\varrho}$ relaxation experiments have been used to explain this observation in terms of preferential localization of the copolymers at the polystyrene/polybutadiene interface [25]. Likewise, the content and length of soft/hard segments and microphase-separated morphology of poly(ether-block-amide) copolymers have been elucidated by and ^{13}C T_1, ^{13}C $T_{1\varrho}$, and ^{1}H $T_{1\varrho}$ relaxation experiments [26]. As a final example, segmented copolymers of poly(N-isopropyl acryl amide) and poly(tetrahydrofuran) have been studied by ^{1}H T_1 and ^{1}H $T_{1\varrho}$ relaxation experiments, to monitor the multiphase characteristics of the segmented copolymer networks as the polymerizable end group of the copolymer was varied [27].

Further, there are numerous examples of how NMR relaxation studies have been exploited to yield practical and useful information about polymer composites. For example, a ^{1}H T_1 and ^{1}H $T_{1\varrho}$ relaxation study of poly(p-phenylene benzobisoxazole) fibers demonstrated the observation of crystalline and noncrystalline regions, and further allowed determination of the crystal size [28]. As another example, the dispersion of organomodified clay fillers in nanocomposites with various thermoplastics was investigated by ^{1}H T_1 relaxation. The comparison in **Figure 9** of the ^{1}H T_1 saturation-recovery curve for polyamide 6 with that of a nanocomposite of polyamide 6

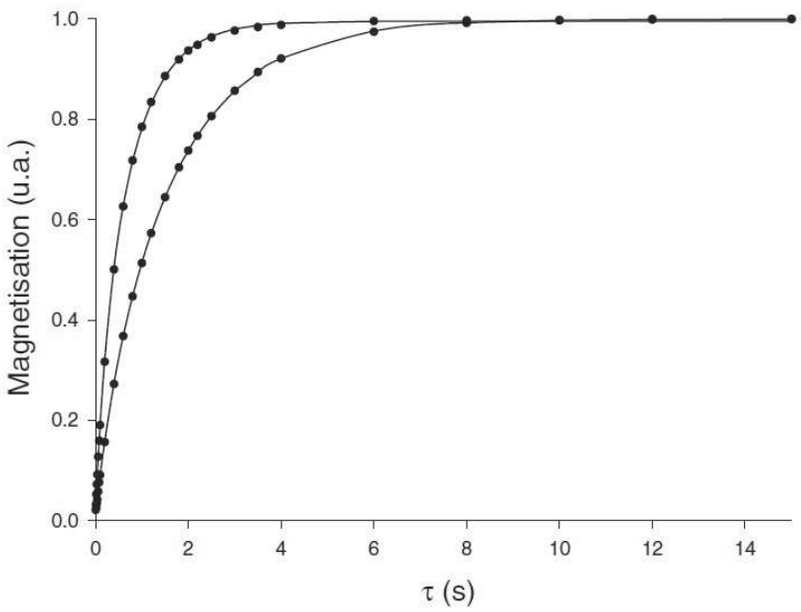

Figure 9. Solid-state ^{1}H T_1 saturation-recovery curves for polyamide 6 and a nanocomposite of polyamide 6 with an organomodified clay. The presence of clay shortens the relaxation time, indicating nanodispersion of the clay in the composite. Reprinted from Ref. [29].

with an organomodified clay, shows that the presence of clay shortens the relaxation time. The nanocomposites have a shorter relaxation time due to paramagnetically induced relaxation at the polymer-clay interface, indicating nanodispersion of the clay. Through a detailed and systematic study thereby, quantitative measurements of the degree of nanodispersion have been made [29].

Finally, in an example involving the combination of copolymers and composites, cotton fibers for composites were modified by surface copolymerization of ethyl acrylate followed by styrene. The graft copolymer-encapsulated cotton fibers were studied by ^{1}H T_1 relaxation experiments, yielding the observation of a heterogeneous morphology of the grafted skin [30].

5. Concluding remarks

Solid-state NMR continues to advance as a valuable technique for characterizing the molecular structure, conformation, and dynamics of polymers. There is already a rich history of applications of various solid-state NMR experiments to numerous polymer systems. Not only are advances occurring in the development of new solid-state NMR techniques, but also techniques which are now considered traditional are finding application to newly developed modern polymer materials. Ultimately, the application of solid-state NMR to polymers provides for the interpretation of spectroscopic observations as related to the structural features and physical properties of the polymer in the solid state, the state in which they are predominately used in as materials.

Author details

Antonio Martínez-Richa[1]* and Regan L. Silvestri[2]

*Address all correspondence to: richa@ugto.mx

1 Universidad de Guanajuato, Guanajuato, Mexico

2 Lorain County Community College, Elyria, USA

References

[1] Koenig JL. Spectroscopy of Polymers. 2nd ed. New York: Elsevier; 1999. 491 p

[2] Saalwachter K, Spiess HW. Solid-state NMR of polymers. In: Moeller M, Matyjaszewski K, editors. Polymer Science: A Comprehensive Reference, Volume 2. Amsterdam: Elsevier; 2012. pp. 185-219. DOI: 10.1016/B978-0-444-53349-4.00025-X

[3] Randall JC. Characterization of long-chain branching in polyethylenes using high-field carbon-13 NMR. In: Woodward AE, Bovey FA, editors. Polymer Characterization by ESR and NMR. Washington DC: American Chemical Society; 1980. pp. 93-118

[4] Sarles LR, Cotts RM. Double nuclear magnetic resonance and the dipole interaction in solids. Physical Review. 1958;**111**(3):853-859. DOI: 10.1103/PhysRev.111.853

[5] Andrew ER, Bradbury A, Eades RG. Nuclear magnetic resonance spectra from a crystal rotated at high speed. Nature. 1958;**182**:1659. DOI: 10.1038/1821659a0

[6] Hartmann SR, Hahn EL. Double nuclear resonance in the rotating frame. Physical Review. 1962;**128**(5):2042-2053. DOI: 10.1103/PhysRev.128.2042

[7] Fyfe CA. Solid State NMR for Chemists. Ontario: CFC Press; 1983. 593 p

[8] Mirau PA. A Practical Guide to Understanding the NMR of Polymers. New York: Wiley; 2004. 418 p

[9] Silvestri RL, Koenig JL. Applications of nuclear magnetic resonance spectrometry to solid polymers. Analytica Chimica Acta. 1993;**283**(3):997-1005. DOI: 10.1016/0003-2670 (93)80261-I

[10] Ernst RR, Bodenhausen G, Wokaun A. Principles of Nuclear Magnetic Resonance in One and Two Dimensions. Oxford: Clarendon Press; 1987. 640 p

[11] Schmidt-Rohr K, Clauss J, Spiess HW. Correlation of structure, mobility, and morphological information in heterogeneous polymer materials by two-dimensional wideline-separation NMR spectroscopy. Macromolecules. 1992;**25**(12):3273-3277. DOI: 10.1021/ ma00038a037

[12] Cao X, Pignatello JJ, Li Y, Lattao C, Chappell MA, Chen N, Miller LF, Mao J. Characterization of wood chars produced at different temperatures using advanced solid-state 13C NMR spectroscopic techniques. Energy Fuels. 2012;**26**(9):5983-5991. DOI: 10.1021/ef300947s

[13] Santonia I, Calloneb E, Sandaka A, Sandaka J, Dirè S. Solid state NMR and IR characterization of wood polymer structure in relation to tree provenance. Carbohydrate Polymers. 2015;**117**:710-721. DOI: 10.1016/j.carbpol.2014.10.057

[14] Takahashi H, Viverge B, Lee D, Rannou P, DePaepe G. Towards structure determination of self-assembled peptides using dynamic nuclear polarization enhanced solid-state NMR spectroscopy. Angewandte Chemie International Edition. 2013;**52**(27):6979-6982. DOI: 10.1002/anie.201210093

[15] Leonard SR, Cormier AR, Pang X, Zimmerman MI, Zhou HX, Paravastu AK. Solid-state NMR evidence for b-hairpin structure within MAX8 designer peptide nanofibers. Biophysical Journal. 2013;**105**(1):222-230. DOI: 10.1016/j.bpj.2013.05.047

[16] Addison JB, Ashton NN, Weber WS, Stewart RJ, Holland GP, Yarger JL. β-sheet nanocrystalline domains formed from phosphorylated serine-rich motifs in caddisfly larval silk: A solid state NMR and XRD study. Biomacromolecules. 2013;**14**(4):1140-1148. DOI: 10.1021/bm400019d

[17] Nieuwendaal RC, Snyder CR, DeLongchamp DM. Measuring order in regioregular poly(3-hexylthiophene) with solid-state 13C CPMAS NMR. ACS Macro Letters. 2014;**3**(2):130-135. DOI: 10.1021/mz4005343

[18] Farrar TC, Becker ED. Pulse and Fourier Transform NMR. New York: Academic Press; 1971. 118 p

[19] Martinez-Richa A, Silvestri RL. Solid-state NMR spectroscopy of multiphase polymer systems. In: Boudenne A, Ibos L, Candau Y, Thomas S, editors. Handbook of Multiphase Polymer Systems. 1st ed. New York: John Wiley and Sons; 2011. pp. 519-549. DOI: 10.1002/9781119972020.ch13

[20] Maeda S, Kunimoto K-K, Sasaki C, Kuwae A, Hanai K. Characterization of microbial poly (ε-L-lysine) by FT-IR, Raman and solid state 13C NMR spectroscopies. Journal of Molecular Structure. 2003;**655**(1):149-155. DOI: 10.1016/S0022-2860(03)00218-7

[21] Asano A, Murata Y, Kurotsu T. Crystallinity and miscibility of poly(vinyl isobutyl ether)/poly(ε-L-lysine) blends by solid state 13C NMR study. e-Journal of Soft Materials. 2007;**3**:1-8. DOI: 10.2324/ejsm.3.1

[22] Spevacek J, Brus J, Divers T, Grohens Y. Solid-state NMR study of biodegradable starch/polycaprolactone blends. European Polymer Journal. 2007;**43**(5):1866-1875. DOI: 10.1016/j.eurpolymj.2007.02.021

[23] Chen W, Feng H, He D, Ye C. High resolution solid-state NMR and DSC study of poly(ethylene glycol)-silicate hybrid materials via sol-gel process. Journal of Applied Polymer Science. 1998;**67**(1):139-147.DOI:10.1002/(SICI)1097-4628(19980103)67:1<139::AID-APP16>3.0.CO;2-X

[24] Phinyocheep P, Saelao J, Buzare JY. Mechanical properties, morphology and molecular characteristics of poly(ethylene terephthalate) toughened by natural rubber. Polymer. 2007;**48**(19):5702-5712. DOI: 10.1016/j.polymer.2007.07.016

[25] Joseph S, Laupretre F, Negrell C, Thomas S. Compatibilising action of random and triblock copolymers of poly(styrene-butadiene) in polystyrene/polybutadiene blends: A study by electron microscopy, solid-state NMR spectroscopy and mechanical measurements. Polymer. 2005;**46**(22):9385-9395. DOI: 10.1016/j.polymer.2005.07.053

[26] Hucher C, Eustache R-P, Beaume F, Tekely P. Motional heterogeneity in poly(ether-block-amine) copolymers as revealed by solid-state NMR. Macromolecules. 2005;**38**(22):9200-9209. DOI: 10.1021/ma051625q

[27] Lequieu W, Van De Velde P, Du Prez FE, Adriaensens P, Storme L, Gelan J. Solid-state NMR study of segmented polymer networks: fine-tuning of phase morphology via their molecular design. Polymer. 2004;**45**(23):7943-7951. DOI: 10.1016/j.polymer.2004.09.024

[28] Bourbigot S, Flambard X, Revel B. Characterisation of Poly(p-phenylenebenzobisoxazole) fibres by solid state NMR. European Polymer Journal. 2002;**38**(8):1645-1651. DOI: 10.1016/S0014-3057(02)00049-6

[29] Samyn F, Bourbigot S, Jama C, Bellayer S, Nazare S, Hull R, Castrovinci A, Fina A, Camino G. Crossed characterization of polymer-layered silicate (PLS) nanocomposite morphology: TEM, X-ray diffraction, rheology and solid-state nuclear magnetic resonance measurements. European Polymer Journal. 2008;**44**(6):1642-1653. DOI: 10.1016/j.eurpolymj.2008.03.021

[30] Castelvetro V, Geppi M, Giaiacopi S, Mollica G. Cotton fibers encapsulated with homo- and block copolymers: Synthesis by the atom transfer radical polymerization grafting-from technique and solid-state NMR dynamic investigations. Biomacromolecules. 2007;**8**(2):498-508. DOI: 10.1021/bm060602w