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Original research paper

Nuclear Magnetic Resonance of Deformed Polymers

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Abstract: Most polymer products are designed to bear mechanical loads. These affect the conformation and mobility of their constituent macromolecules. Nuclear magnetic resonance (NMR) is sensitive to molecular conformation and mobility and has been employed to study the signature of macroscopic deformation of polymer materials on a scale ranging from molecular to macroscopic dimensions. This report reviews key studies of polymer deformations by NMR spectroscopy, relaxometry, and imaging.

Keywords: NMR, relaxometry, imaging

शोधसार: धैरैजसो पोलिमर उत्पादनहरू यांत्रिक भार सहन सक्ने गरी डिजाइन गरिएका हुन्छन्। यस्ता भारहरूले तिनीहरूको संरचनात्मक म्याक्रोमोलेक्युलहरूको आकृति र गतिशीलतामा असर पार्दछ। न्युक्लियर म्याग्नेटिक रेजोनेन्स (NMR) प्रविधि आणविक आकृति र गतिशीलताको लागि संवेदनशील हुन्छ, र यसलाई पोलिमर सामग्रीको आणविकदेखि म्याक्रोस्कोपिक स्तरसम्मको बस्तुको संरचनामा हुने रुपान्तरणको अध्ययन गर्न प्रयोग गरिएको छ। यो प्रतिवेदनले NMR स्पेक्ट्रोस्कोपी, रिल्याक्सोमेट्री, र इमेजिङ प्रयोग गरी पोलिमरको संरचनामा हुने रुपान्तरण तथा संरचनात्मक विकृति सम्बन्धी गरिएका प्रमुख अनुसन्धानहरूलाई समेट्छ।

INTRODUCTION

Polymer materials are formulated from macromolecules, processing and antiaging additives, plasticizers, and fillers [1-4]. Their main constituent are the macromolecules. These are large molecules, most often chains of small molecular repeat units, typically with branches, and some with cross-links to other chains. Elastomers are the most important representative of cross-linked macromolecules in the molten or rubbery state. Technical macromolecules are not uniform like small molecules but exhibit distributions in molecular weight and configuration in terms of branches and sequences of repeat units if there is more than one repeat unit or if the same repeat units are connected in different ways.

Polymer materials are often classified according to the conformation of the macromolecules in the solid state. In the melt, the macromolecular chains form random, interpenetrating coils with free volume between chains, which enables translational motions of entire chains and local motions of chain segments. The melt freezes upon cooling below the glass transition temperature. In the frozen melt, the translational motion of entire chains is largely disabled while local motions persist. Such amorphous polymers typically are transparent and are called glassy polymers. Strictly speaking, they are not in thermodynamic equilibrium, and given enough time, chain segments can still slip past each other, particularly under pressure or strain, unless the chains are crosslinked. The nature of cross-links can be either chemical, i. e., the cross-links are formed by chemical bonds, or physical, i.e., the macromolecules are physically entangled through loops and knots or linked through crystalline domains formed by two or more polymer chains.

Partially crystalline polymers are called semicrystalline, and their crystalline domains may form ordered structures, for example, lamellae. The term crystalline polymer is used synonymously with semicrystalline polymer, as single crystals of large macromolecules are difficult to grow. The mobility of the polymer chain segments in the amorphous regions is higher, along with more free volume, while it is lower in the crystalline regions and mostly located at crystal defects. At the interface from ordered crystalline domains to disordered amorphous domains, the segmental

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chain mobility transitions from low to high. Molecular order also arises in polymer melts under shear and in liquid-crystalline polymers. It is directly probed by diffraction patterns from x-ray scattering and by wide-line solid-state NMR (nuclear magnetic resonance) spectroscopy. It is indirectly probed via molecular mobility, for example, by NMR relaxometry.

NMR probes the magnetic moments of nuclear spins in molecules exposed to magnetic polarization fields. It has three major modalities, spectroscopy, imaging, and relaxometry [5]. NMR spectroscopy of molecules in solution is one of the most important methods of chemical analysis for identification of molecular structures [6]. With molecules in the solid state, NMR spectroscopy for chemical analysis is hampered by various anisotropic interactions between the nuclear spins. But the rapid thermal molecular motion prevalent in solution can be artificially replaced in solids by rapid rotation of the entire solid sample at a particular angle relative to the direction of the applied magnetic field. This technique is known as magic angle spinning (MAS) NMR and leads to solid-state spectra with lines nearly as narrow as in liquid-state NMR spectra. On the other hand, the anisotropic spin interactions can be exploited to probe molecular order and mobility [7]. To this end, many studies of solid polymers have been conducted by recording wide-line deuteron (^{2}H) NMR spectra from selectively deuterated chemical positions of interest. These spectra are much broader than the lines in MAS spectra, because each molecular orientation in the magnetic field gives rise to a different NMR frequency.

Solid-state NMR spectra are recorded with expensive NMR instruments fitted with high-field

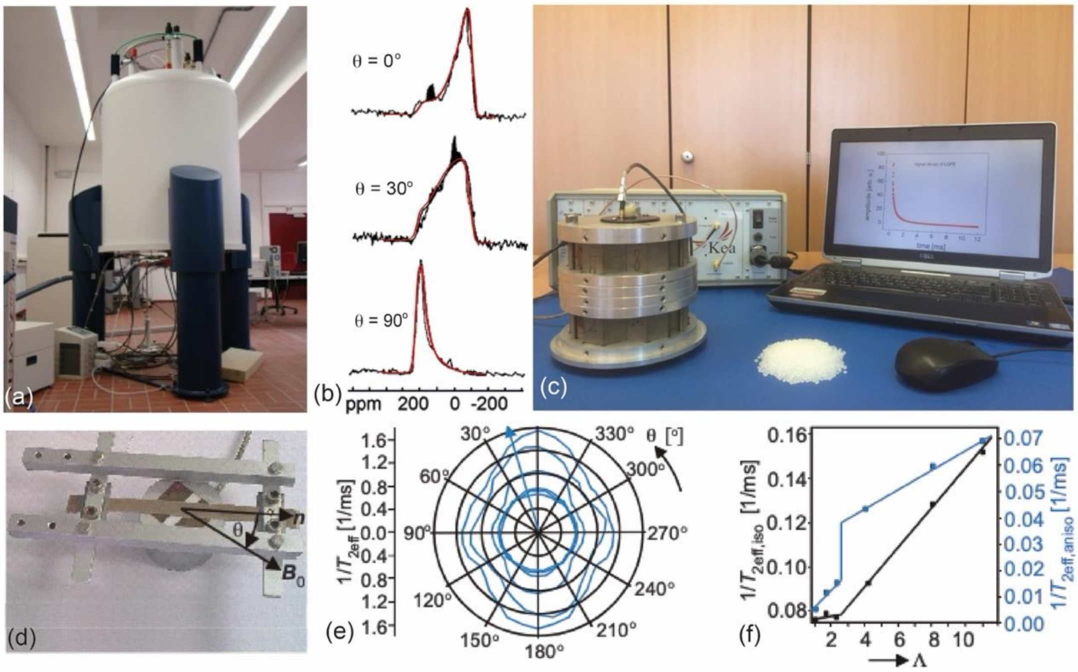

Figure 1. (a) Magnet of an 800 MHz spectrometer for chemical analysis by NMR spectroscopy [5]. (b) Orientation-dependent ^{13}C wide line NMR spectra of a ^{13}C-labeled liquid-crystalline sidechain polymer with different orientation angles θ between the alignment direction and the magnetic field [8]. (c) Low-field NMR set-up for measurement of NMR relaxation signals [5]. The sample is positioned inside the permanent magnet (left). A transverse NMR relaxation curve (red) is shown on the computer screen. (d) Strained rubber band positioned on a stray-field magnet (NMR-MOUSE [9]) for angle-dependent relaxation measurements [5]. (e) Strain and angle-dependent relaxation rates measured for unfilled natural rubber [10]. With increasing strain, the relaxation anisotropy increases. (f) Isotropic and anisotropic relaxation rates extracted from (e) as a function of elongation Λ [5].

top instruments, which are considerably less expensive and simpler to operate [11]. Compact as well as portable or mobile

NMR instruments also exist for measuring NMR relaxation signals (Fig. 1c) [12,13]. NMR relaxation does not provide molecular information about the chemical nature of a substance, but instead it provides mesoscopic information about the physical properties of a material. It refers to the NMR relaxation times T_1 and T_2 characterizing build-up and decay of nuclear magnetization [14], which relate to the mobility of molecules and, in turn, to the viscoelastic properties of matter [15]. NMR relaxometers are less demanding on magnet performance than NMR spectrometers; they are more robust and can be operated in harsher environments. While most benchtop NMR instruments require a sample to be fitted inside a center hole of a permanent magnet (Fig. 1c), portable instruments acquire essentially the same information locally from a selected region inside intact objects by facing them from one side (Fig. 1d) [16]. When shifting the sensor relative to the object, images can be acquired pixel by pixel.

NMR imaging (MRI – magnetic resonance imaging) is a modality of NMR where spatial resolution is introduced by means of magnetic gradient fields [17-19]. NMR images report molecular properties visually on a macroscopic scale. The main use of MRI is in clinical diagnostics, but it is also employed to a considerable extent in materials science, chemical engineering, and related fields [13,20-23], including rheological studies of complex fluids [24].

All three NMR modalities, spectroscopy, relaxometry, and imaging have been explored to investigate the effects of mechanical force on polymer materials. In the following, major contributions of the NMR literature in this field are reviewed for different types of macromolecular materials.

RUBBERY MATERIALS

Basic NMR

Rubber is a melt of entangled macromolecules. Crosslinking inhibits translational motion of the macromolecules, so that they can no longer diffuse and slip past each other. Active fillers like carbon black strongly interact with the macromolecules and affect their segmental motion near the filler-particle surface and significantly alter the mechanical properties of the material. Between crosslinks the motion of the macromolecular chains is fast reminiscent of the motion in a low-molecular melt, but anisotropic so that orientation-dependent spin interactions like the dipole-dipole coupling among protons and the quadrupolar coupling of deuteron spin labels are no longer averaged out. Rubbery materials have been studied extensively by NMR to understand their structural and dynamic properties and the effects of strain, exploring the orientation-dependent residual dipolar and quadrupolar couplings.

In the relaxed state without deformation, the ^{1}H NMR resonance of elastomers is broadened compared to that of liquids due to the molecular motion being constrained by crosslinks and entanglements between polymer chains. As a result, the information attached to the chemical shift is blurred and mostly lost so that most investigations concern the ^{1}H NMR signal decay in the time domain or the transverse magnetization decay, while spectral analyses rely on other nuclei such as ^{13}C with a far wider chemical shift range and on ^{2}H after site-specific isotope enrichment.

^{1}H relaxometry

Models of the ^{1}H NMR signal decay of cross-linked rubber account for different motional regimes in the rubber network [25-27]. Depending on the model, different simplifying assumptions are made in calculating the ^{1}H signal decay [28]. The frozen-bond model assumes that all crosslink positions in a network are immobile and that the end-to-end vectors of the inter-crosslink chains have a Gaussian distribution [29–31]. The second-moment model assumes a Gaussian distribution of dipolar interactions and an exponential correlation function of the segmental motion [32]. Both models can explain the non-exponential nature of the NMR impulse response, specifically the free induction magnetization decay (FID) of the amplitude in the Hahn-echo NMR experiment [28]. Yet for practical purposes a simple approximation of the signal decay in terms of a sum of three relaxation decays often suffices, in which the individual terms account for the more fixed inter-crosslink chains, for dangling chains and for the sol part.

Fitting theoretical relaxation decays to experimental data gives access to the cross-link density [33,34]. Its variation across an elastomer product can be assessed by NMR imaging [35,36] or depth-resolved stray-field NMR relaxometry [9,37,38]. Approaches to cross-link density and other material parameters more sophisticated than simple relaxation analyses explore multi-quantum phenomena resulting from the residual dipole-dipole interactions among the protons in randomly oriented inter-crosslink chains [39-42].

Upon straining, the motional anisotropy of the intercross-link chains is enhanced, and the signal decay changes from more liquid-like to more solid-like [25-27]. This means that the chemical shift anisotropy, the dipole-dipole interaction among nuclear spins, and the quadrupole couplings of ^{2}H isotope labels are enhanced because the molecular motion is averaged to a lesser degree. In the deformed regions, the macromolecular chains align so that the overall NMR signal depends on the orientation of the alignment direction with respect to the applied magnetic field [31,43]. Not only can an orientation-dependent splitting of the resonance line be observed, but also the NMR relaxation times become anisotropic. While the dependence of the NMR signal on strain and time in terms of relaxation times and component amplitudes can be followed with moderate effort employing a conventional NMR setup, where the sample is positioned in the center inside an NMR magnet [44], to study the orientation dependence of the NMR signal requires the angle between the strain direction and the magnetic field to be varied. This can be achieved either with the sample and the stretching device inside the confinement of the NMR magnet or with a simple stray-field setup using a sensor like the NMR-MOUSE (MObile Universal Surface Explorer), where the strained sample rests on the magnet, and the NMR signal is acquired from a region inside the sample but outside the magnet (Fig. 1d) [9,10]. When approximating the signal decay of the strained elastomer by a single exponential function, the orientation dependence of the transverse relaxation rate in natural rubber (Fig. 1e) can be modelled by the sum of an orientation-independent relaxation rate and a relaxation rate which depends on the square of the second Legendre polynomial. With increasing strain, both relaxation rates increase albeit at different rates (Fig. 1f). At an elongation of about $\Lambda = 2.3$, strain-induced crystallization sets in. At this elongation the anisotropic relaxation rate exhibits a first order phase transition as a function of Λ while the isotropic relaxation rate changes in a way reminiscent of the glass transition or a second order phase transition [45]. Strain-induced crystallization has been investigated by NMR relaxometry and multi-quantum NMR for natural rubber and polyurethane elastomers [46,47].

Along with chain alignment, mechanical deformation alters segmental mobility, affecting proton transverse relaxation [48-50] and relaxation dispersion [50] as well as multipolar spin states [51] and multi-quantum build-up curves [39-42]. Fillers enhance mechanical reinforcement but introduce heterogeneous strain fields. They affect local strain distributions and overstrain phenomena [52,53]. Reinforced elastomers exhibit non-affine deformation, where local strain does not follow macroscopic deformation. In solid propellants, ^{1}H NMR relaxometry identifies deformation-induced microstructural changes [54]. In thermoplastic elastomers, deformation influences the microphase-separated structure of the copolymers, affecting chain dynamics and relaxation times [48].

^{13}C NMR spectroscopy

Effects of strain are also observable in NMR spectra of ^{13}C in natural abundance and of ^{2}H isotope labels enriched at selected chemical sites. ^{13}C NMR spectra of strained rubber exhibit broadened lines which depend on the sample orientation in the magnetic field [55,56]. While the ^{1}H-^{13}C dipole-dipole interaction is suppressed during measurement, the ^{13}C-^{13}C dipole-dipole coupling is negligible due to the low natural abundance of the nuclei, but the large ^{13}C chemical shift range enables the chemical shift anisotropy to be resolved, leading to small variations in resonance frequencies for different chain-segment orientations. In natural rubber, the efficiency of transferring ^{1}H magnetization to ^{13}C by cross-polarization was affected by strain-induced chain orientation, revealing a time-dependent mechanism of chain-segment dynamics on dynamic strain [57], and strain-induced crystallization was studied by high-resolution solid-state ^{13}C NMR spectroscopy of natural rubber samples stretched *in situ* [58].

^{2}H NMR spectroscopy

The most detailed insights by NMR into the molecular dynamics and structural characteristics of strained or deformed elastomers are obtained by analyzing the resonance of chemical sites specifically enriched with deuteron isotope labels. ^{2}H is a quadrupolar spin 1 nucleus which exhibits orientation-dependent line shapes on the order of 2 kHz wide in elastomers and up to 250 kHz wide in rigid polymers, dominating the dipole-dipole coupling and the chemical shift anisotropy [59,60]. From fits of modelled to measured line shapes, the orientational distribution function, geometry, and timescale of molecular motion can be extracted. Two-dimensional NMR experiments are particularly powerful in this regard [60].

Early on, this chemically demanding approach was employed to study the effects of deformation on chains in rubber-elastic networks. Strain, but also compression, leads to strain-dependent splitting of the ^{2}H NMR resonance due to average uniaxial chain orientation under strain [61-64]. Experiments on homogeneously deuterated networks and on partially deuterated networks with short deuterated segments at network junctions revealed a nonaffine deformation mechanism where short elastically effective chains are stretched to a greater extent than long chains along with an excess orientation near network junctions [2,65]. By analyzing the ^{2}H NMR line shape, the contributions from the network constraints and the chain interactions to the average orientation of the chain segments can be separated, and the average molecular weight between topological constraints be calculated [66,67]. Moreover, ^{2}H NMR spectroscopy reveals that the molecular dynamics along the cross-link chain are heterogeneous and more restricted in the junction zones [68,69]. Consequently, effects of chain orientation from strain are stronger in the center of cross-link chains than near the cross-link points [70]. Similar heterogeneity of molecular dynamics is produced by active fillers, where local chain mobility is slowed down in an adsorption layer [72]. A relatively small fraction of chains strongly absorbed to active fillers impacts the stress-strain properties of filled elastomers significantly [72].

The chemical labelling effort is avoided, if deuterated network-like chains are incorporated into the elastomer sample by swelling prior to measurement [73-75]. In this way, stress-induced crystallization and melting have been studied in natural rubber with and without carbon black filler [76,77]. The segmental order observed upon dilution, however, depends on the solvent. The chain order is less affected by chain oligomers as solvents than with conventional low molecular weight solvents [78]. Yet the anisotropy of the cross-linked network suffices even in stretched poly(dimethyl siloxane) gels to slightly align biomolecules so that their residual dipolar couplings can assist the effort to unravel their molecular structures [79-81].

Magnetic resonance imaging

NMR imaging (MRI – Magnetic Resonance Imaging) is a nondestructive method particularly suited to obtain 3D and 2D tomographic images of soft matter [17,18]. It has become an indispensable diagnostic tool in medicine, complementing X-ray tomography by its abundance of contrast parameters for soft matter diagnosis. The synthetic equivalence to biological soft matter is rubber and elastomers, so that early on, MRI has been explored to study rubbery materials, with particular attention to variations in crosslink density, filler distribution, solvent ingress, and aging [20,35,36]. While on a sufficiently coarse scale rubbery materials are considered homogeneous, the NMR signal from sufficiently small volume elements reveals variations in cross-link density and filler content, an observation to be expected when considering the statistical nature of their distributions. Already, the voxel volume of MRI and even stray-field NMR is small enough to be sensitive to such inhomogeneities [82]. Additional inhomogeneities arise from insufficient mixing during product manufacturing [83], so that MRI, along with stay-field NMR relaxometry, are valuable assets in rubber process control and manufacturing [84]. Large products do not fit into the MRI magnet, and those containing steel, like most tires, are unfit because of their interaction with the magnet. While the use of rubber MRI is mainly of interest in research, stray-field NMR relaxometry is well integrated in parts of the tire industry [9,37,38].

An early MRI study revealed that the spatial distributions of the ^{1}H spin density is lowered and the molecular motion of water molecules in a gel is slowed down by compression compared with those in the surrounding uncompressed region [85]. A filled polysiloxane rubber band with a cut was imaged under elongation [83]. The filler distribution was found to be inhomogeneous, and images of the transverse relaxation time were calibrated to report stress and strain maps. Local strain has also been mapped by means of deuterated spy oligomers incorporated into the object and making use of their strain-dependent double-quantum signal or the ^{2}H line splitting, as has been demonstrated with deuterated poly(butadiene) oligomers incorporated into a natural rubber band with cuts [86,87]. The same information can be obtained without sample preparation by mapping different multi-quantum NMR parameters associated with the strain-dependent residual ^{1}H-^{1}H dipolar coupling [88,89]. In a comparative study, MRI and stray-field relaxometry with the NMR-MOUSE were found to reveal differences in molecular mobility in silicone elastomers arising from differences in cross-link density, material heterogeneity, aging, and strain [90]. Moreover, the impact of radiation on the shear modulus of silica-filled PDMS elastomers was quantified by ^{1}H relaxation measurements and stray-field imaging [91].

Depending on the loss modulus, the mechanical energy imparted to the rubber material by dynamic mechanical load raises the temperature. The thermal energy is dissipated through the surface of the object, leading to a temperature distribution inside. The distributions of molecular mobility associated with different carbon-black filler contents of dynamically sheared rubber cylinders were reported by parameter images of the transverse relaxation time and recalibrated to temperature distributions [92].

In a unilateral stray-field NMR setup, oscillation-synchronized NMR excitation served to extract the deformation waveforms in different viscoelastic polyurethane samples, which were then processed to calculate the loss-angle and magnitude of the dynamic modulus for each sample [93]. Mechanical motion, like oscillatory or viscous fluid shear, can well be studied by MRI and unilateral stray-field NMR. The underlying NMR methodology and instrumentation have recently been reviewed in the literature with particular attention to portable stray-field NMR, which provides open access to the sample for mechanical deformation accessories [94].

By means of magnetic field gradients oscillating with the same frequency as the mechanical deformation, the propagation of mechanical waves can be imaged, and their interference patterns can be analyzed, giving access to maps of the storage and loss moduli across an object [18]. This approach is termed NMR elastography. It can be employed for elastomers [95–98] but more importantly, it is of considerable interest for diagnosing cancer in living tissue [99–103].

RIGID POLYMERS

^{1}H relaxometry

Rigid polymers are predominantly in the amorphous, glassy state below the glass transition temperature or the semicrystalline state between the glass transition temperature and the melting temperature. The amorphous regions usually are characterized by higher segmental mobility and larger free volume than the defect-bearing crystalline regions. They are commonly understood to respond to increasing mechanical deformation before the crystalline domains are affected, leading to strain hardening, brittle or ductile behavior depending on the deformation rate and temperature, and crazing until failure [104,105]. ^{1}H NMR relaxation studies are also well suited to investigate the impact of deformation and aging in solid polymers, because these phenomena primarily affect the segmental mobility on a time scale to which NMR relaxation is sensitive.

Mobile, single-sided NMR relaxometry is a unique tool for investigating the effects of polymer aging, deformation and annealing, which has been demonstrated on a variety of technologically relevant materials like LDPE (low density poly(ethylene)) steel-pipe shells, HDPE (high density poly(ethylene)) pipes, polypropylene, and Nylon 6 [106–111]. The NMR signal decay of a semicrystalline polymer can be decomposed into three different components, which are attributed in decreasing order of the relaxation times to the amorphous, interfacial, and crystalline domains constituting the material morphology. In uniaxially stretched poly(propylene), both the relaxation times of the amorphous and the interfacial regions decreased with increasing elongation while the amorphous content increased, and the interfacial and crystalline contents decreased [109]. Similarly, a recent, combined study of the amorphous-chain reorientation under uniaxial elongation of low-density polyethylene relying on wide-angle X-ray scattering data and orientation-dependent solid-state NMR signal decays revealed the formation of additional rigid amorphous regions above a threshold elongation [112]. On the other hand, in a weakly curved, carbon-black-filled PE pipe section, both the relaxation times of the amorphous and the interfacial regions increased upon straining the pipe [106,108|.

NMR spectroscopy of ^{2}H and ^{13}C isotope labels

Enhanced chain mobility was also observed by deuteron NMR in the amorphous regions of deuterated Nylon 6 under active uniaxial deformation near the glass transition temperature, which relaxed upon stress release [110], whereas the mobility of D_2O incorporated into Nylon-6 became progressively confined with increasing alignment of polymer chains and strain-associated changes in polymer morphology [111].

Strain-enhanced molecular mobility is also expected from molecular dynamics simulations for glassy polymers [113,114]. This has been observed by ^{2}H NMR for bulk polycarbonate and poly(*p*-phenyleneterephthalamide) fibers [115–118]. Wideline ^{2}H 2D exchange NMR spectroscopy of phenyl-ring deuterated polycarbonate revealed that the reorientation angle distribution of the phenyl-ring flip widened upon stretching the sample inside the NMR magnet with a dedicated titanium rig [117]. Subsequently, enhanced phenyl ring dynamics were observed by the same method in poly(*p*-phenyleneterephthalamide) fiber bundles uniaxially loaded to 55% of their breaking strength [116]. Moreover, double quantum correlated 2D NMR spectroscopy on doubly ^{13}C labeled polycarbonate confirmed that the geometry of the entanglement network is the most important structural parameter for the plastic behavior of glassy polymers [117]. The conformational distribution was found to be unaffected by the deformation, whereas small changes in the local packing of molecular segments could be detected in terms of the phenylene ring planes tending to orient parallel to one another upon deformation [118]. The same experimental technique revealed that the degree of molecular alignment in dragline silk fibers increases with the fiber draw rate, and that it changes more, when the drawing tension on the fiber is relaxed from higher draw rates [119]. Wideline ^{13}C NMR spectra were also measured to follow the light-induced change in orientational order of an oriented liquid-crystalline side-chain polymer film (Fig. 1b) [8].

NMR imaging

NMR imaging of rigid polymers is challenged by short transverse relaxation times, which require special solid-state imaging techniques, unless images of the soft fractions suffice. Else, high excitation power, small samples, and line-narrowing techniques like MAS (magic angle spinning) or isotope enrichment of the sample need to be applied [18,120–122]. Information on molecular order and dynamics can be extracted from spatially resolved wide-line spectra of samples labelled by ^{2}H at selected chemical sites when the spatial information is encoded in the narrow double quantum resonance, an approach which has been demonstrated on a phantom constructed from drawn poly(ethylene) [123,125]. On the other hand, the ^{13}C resonance is sufficiently narrow to enable space encoding, albeit at the expense of long measurement times due to the low natural abundance of the nucleus. This has been demonstrated with a spectroscopic ^{13}C image of a tensile bar from syndiotactic poly(propylene), which revealed the skin-core layer structure of the object that resulted from the orientation and associated inhomogeneous cooling of the material during injection molding [124,125].

Special multi-pulse NMR line-narrowing sequences can sufficiently extend the duration of the ^{1}H NMR signal for space encoding and give access to relaxation rates sensitive to defect structures in rigid polymers. In this way, polycarbonate samples drawn to different elongation ratios up to $l = 2.7$ have been imaged with the multi-pulse relaxation time as a contrast parameter [126]. In the necking region, the relaxation rate was increased due to immobilization of the small amplitude phenylene motion corresponding to a temperature shift of 10 K. Moreover, two crossing shear bands were clearly visible in an NMR image, whereas they were far less resolved in a polarization microscopy image.

In a detailed study, ^{1}H NMR imaging served among others to yield the chain director distribution in macroscopic sections derived from a frozen contraction flow of a main-chain liquid crystalline polymer [127]. The crack-growth resistance of ABS, a blend of poly(styrene-*co*-acrylonitrile) with poly(butadiene) and PBT/PTMO, a block copolymer of poly(butylene terephthalate)/poly(tetramethylene oxide) was studied by ^{1}H MRI of the crack tip with a dedicated stretching device that allowed to keep notched materials under load inside the magnet during imaging [128]. Numerous damage bands appeared in the images of strained ABS, which converged toward the crack tip and remained upon unloading. The image contrast was due to reduced material density. With the same setup, notched specimens of two different types of extruded polyamide 6 and maleic anhydride grafted ethylene-propylene blends were examined under critical load, where one blend contained pure rubber particles dispersed in the PA6 matrix, and the other contained PA6 occlusions within the rubber particles [126]. MRI experiments revealed a gradual increase of rubber cavitation toward the crack tip, whereby the tougher blend with the occlusions had a significantly more extended plastic zone ahead of the crack tip.

SUMMARY

Mechanical deformation of polymer materials changes the mobility and alignment of their constituting macromolecules. These properties can be probed by NMR in terms of NMR relaxation times and resonance frequencies. Relaxation times are primarily determined by molecular motion, whereas resonance frequencies are determined by the impact of average molecular order on anisotropic spin interactions between ^{1}H nuclei, ^{13}C chemical shifts, and ^{2}H isotope labels. The NMR modalities of spectroscopy and relaxometry have been employed individually and combined with spatial resolution in NMR images to unravel many details of the molecular response to strain and pressure on a space scale ranging from the chain segment to a macroscopic sample section. While the execution of most NMR techniques demands the skills of experts, NMR relaxometry inside and outside the magnet is simple to use and has found its way to elastomer manufacturing sites, providing valuable information on cross-link density, quality of mixing, and aging. Investigations of the polymer response to static and dynamic strain, on the other hand, have greatly contributed to the principle understanding of the impact of deformation on molecular dynamics, order, and polymer morphology on the way to real-time monitoring of polymer processing steps and the conception of ecologically sound, smart, and responsive polymer materials.

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