Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials

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1. Introduction

This article reviews the principles and applications of one of the currently most powerful NMR approaches for the characterization of chain motion in elastomers, entangled

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Nomenclature

List of symbols, abbreviations and acronyms

ACF	autocorrelation function
$a(\psi)$	duty-cycle dependent scaling factor
AW	Andersen–Weiss
BR	butadiene rubber
C_∞	Flory's characteristic ratio
$C(t)$	orientation autocorrelation function
CPMG	Carr–Purcell–Meiboom–Gill
DCC	dipolar coupling constant
DCE	dipolar correlation effect
DELM	dipolar-encoded longitudinal magnetization
DLS	dynamic light scattering
DSC	differential scanning calorimetry
DQ	double quantum
D_{eff}	effective DCC ($=D_{stat}/k$)
D_G	residual DCC, Gaussian distribution average
D_{res}	residual DCC
D_{stat}	static-limit DCC
Δ_i	inter-pulse spacing
FID	free induction decay
$\bar{H}_{DQ}$	average (DQ) Hamiltonian
$\hat{H}_J$	(J coupling) Hamiltonian
I	spectroscopic intensity
$\hat{I}_{+/-}^{(i)}$	raising/lowering spin operator
J	scalar coupling
k	scaling factor for the intra-segmental DCC
κ	power-law exponent
LM	longitudinal magnetization
M_{2eff}	effective static-limit second moment
M_{2res}	residual second moment
M_c	network chain molecular weight
M_e	entanglement molecular weight
M_{te}	molecular weight between trapped entanglements
MAS	magic-angle spinning
MQ	multiple quantum
N	number of statistical (Kuhn) segments
n_c	number of pulse sequence cycles
nDQ	point-by-point normalized DQ intensity
NR	natural rubber (poly(cis-1,4-isoprene))
$P(\ldots)$	probability density
$P_2(\ldots)$	second Legendre polynomial
PB	poly(butadiene)
PDMS	poly(dimethylsiloxane)
phr	per hundred rubber
PS	poly(styrene)
PS-b-PB	PS-block-PB copolymer
P(S-co-AMS)	poly(styrene-co-aminomethylstyrene)
$\Phi_{\ldots}$	pulse phase
$\phi_{\ldots}$	integrated dipolar evolution phase
Q	degree of volume swelling V/V_0
RDC	residual dipolar coupling
REDOR	rotational-echo double-resonance
SBR	styrene–butadiene rubber
S_b	dynamic order parameter of the polymer backbone
$\sum$MQ	multiple-quantum sum intensity
σ_G	standard deviation of Gaussian distribution
SEDOR	spin–echo double resonance
T_2^*	apparent transverse relaxation time
T_g	glass transition temperature
t_p	90° pulse length
t_c	pulse sequence cycle time
τ_{DQ}	DQ evolution time
τ_d	disengagement or terminal relaxation time
τ_e	entanglement time
$\tau_{f/s}$	fast/slow correlation time
τ_R	(longest entanglement-constrained) Rouse time
τ_z	z-filter time
WLF	Williams–Landel–Ferry
ZQ	zero quantum

polymer melts and related mobile polymeric systems well above the glass transition. Considering the ubiquitous applications of rubbers, as well as the industrial relevance of melt processing of polymers, the rheological behavior of soft polymeric systems is of central (technological) concern, yet the establishment of quantitative relationships between macroscopic properties and structure and dynamics at the molecular level remains an open challenge.

Melt-like polymer chains exhibit a complex hierarchy of dynamic processes, starting with very fast and local conformational rearrangements on the ps scale, and extending into the range of seconds for slow, diffusive and cooperative motions [1]. Fast local motions are the domain of NMR methods based on longitudinal spin relaxation of suitable nuclei such as protons or carbon-

13, where the study of the relaxation dispersion over a large frequency range for the former via field-cycling methods [2–5] or the chemical resolution of the latter [6,7] are the basis of the most powerful strategies, and do not even require isotopic labelling. This class of methods is not covered here and the reader is referred to the cited literature.

Motions that involve a larger number of segments up to the level of whole chains dominate the mechanical properties of soft polymeric systems, emphasizing the need for NMR methods that are sensitive in the corresponding frequency range. Traditionally, transverse relaxation phenomena of protons or deuterons, or, equivalently, line shape analysis in the frequency domain, have been used for that purpose [8–20], and provided the starting point for more