

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

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