Transreactions in Condensation Polymers

Stoyko Fakirov (Ed.)

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Prof. Dr. Stoyko Fakirov
Lab. Structure and Properties of Polymers
University of Sofia
1 James Bourchier Blvd.
1126 Sofia
Bulgaria

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Contributors

Aerdts, A. M.
Eindhoven University of Technology,
Laboratory of Polymer Chemistry and Technology,
P. O. Box 513, 5600 MB Eindhoven, The Netherlands

Baltá-Calleja, F. J.
Institute of Structure of the Matter, CSIC,
Serrano 119–123, 28006 Madrid, Spain

Berti, C.
Department of Applied Chemistry and Materials Science,
University of Bologna,
Viale Risorgimento 2, 40136 Bologna, Italy

Blackwell, J.
Department of Macromolecular Science,
Case Western Reserve University,
Cleveland, OH 44106-7202, USA

Denchev, Z.
Faculty of Chemistry, Laboratory on Polymers, Sofia University,
1 James Bourchier Ave., 1126 Sofia, Bulgaria

Devaux, J.
Catholic University of Louvain,
Faculty of Applied Sciences,
Laboratory of Chemistry and Physics of High Polymers,
Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

Economy, J.
Department of Materials Science and Engineering,
University of Illinois at Urbana-Champaign,
1304 West Green Street, Urbana, IL 61801, USA

Eersels, K. L. L.
Catholic University of Leuven (KULeuven),
Department of Chemistry,
Laboratory for Macromolecular Structural Chemistry,
Celestijnenlaan 200F, B-3001 Heverlee, Belgium

Fakirov, S.
Faculty of Chemistry, Laboratory on Polymers, Sofia University,
1 James Bourchier Ave., 1126 Sofia, Bulgaria

Fiorini, M.
Department of Management, Research Unit on
Technology and Resources, University of Bologna,
Piazza Scaravilli 2, 40126 Bologna, Italy

Frich, D.
ARCO Chemical Co., Technical Center,
South Charleston, WV 25303, USA

Groeninckx, G.
Catholic University of Leuven (KULeuven),
Department of Chemistry,
Laboratory for Macromolecular Structural Chemistry,
Celestijnenlaan 200F, B-3001 Heverlee, Belgium

James, N. R.
Division of Polymer Chemistry, National Chemical Laboratory
Pune 411008, India

Kricheldorf, H. R.
Institute for Technical and Macromolecular Chemistry,
Hamburg University,
Bundesstrasse 45, 20146 Hamburg, Germany

Mahajan, S.
Division of Polymer Chemistry, National Chemical Laboratory
Pune 411008, India

McCullagh, C. M.
Department of Macromolecular Science,
Case Western Reserve University,
Cleveland, OH 44106-7202, USA

Montaudo, G.
Department of Chemistry, University of Catania,
Viale A. Doria 6, 95125 Catania, Italy

Pilati, F.
Department of Chemistry, University of Modena,
Via Campi 183, 41100 Modena, Italy

Puglisi, C.
Institute for Chemistry and Technology of Polymeric Materials,
National Council of Research,
Viale A. Doria 6, 95125 Catania, Italy

Samperi, F.
Institute for Chemistry and Technology of Polymeric Materials,
National Council of Research,
Viale A. Doria 6, 95125 Catania, Italy

Schneggenburger, L. A.
Department of Materials Science and Engineering,
University of Illinois at Urbana-Champaign,
1304 West Green Street, Urbana, IL 61801, USA

Sivaram, S.
Division of Polymer Chemistry, National Chemical Laboratory,
Pune 411008, India

Warth, H.
Bayer AG, Plastics Business Group,
D-41538 Dormagen, Germany

Xanthos, M.
Polymer Processing Institute,
Hoboken, NJ 07030, USA

and: NJ Institute of Technology,
Department of Chemical Engineering,
Chemistry and Environmental Science,
Newark, NJ 07102, USA

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Preface

An inherent property of condensation polymers, in contrast to polyolefins, is their ability to react with each other. Regardless of the mechanism of the chemical reactions during polymer synthesis, the presence of groups of ester, amide, urethane, and other similar types, as well as carboxylic, amine, *etc.*, groups in the macromolecules makes the post reactions possible.

The practical importance of these reactions was first recognised by Flory, who got his patent in 1939 for molecular weight upgrading of polyamide 6 by means of solid state post-condensation. In his fundamental book, he analysed for the first time the constructive and destructive reactions in condensation polymers and their blends. Later, the attention of polymer chemists and physicists was focused on much more attractive problems of polymer science. For the chemists the additional condensation and transreactions seemed to be rather primitive, while physicists hardly knew about their existence, although they always took place during such a "purely" physical treatment as annealing at temperatures close to melting. These reactions attracted again the attention of polymer scientists by the start of intensive studies of polymer blends. It turned out that immiscibility and incompatibility could be overcome to a great extent by producing thin copolymer layers at the interface of blends of condensation polymers, mostly *via* transreactions.

The ability of condensation polymers to undergo additional chemical reactions is fascinating. These reactions allow one (i) to prepare novel copolymers with desired composition and sequential order, as well as to enhance compatibility, (ii) to obtain more uniform polymers by minimising molecular weight fluctuations in a melt stream during polycondensation and processing and (iii) to provide for chemical healing of laminates of condensation polymers.

A good friend of mine, who is a polymer physicist with world-wide reputation, does not believe that transreactions really exist. When, by chance, I told this to another common friend, who is a famous polymer chemist, his reaction was, "Tell him that Professor Flory, with whom he worked so many years, would be very unhappy if he could hear his statement". As a matter of fact, this was the first very strong impulse for starting this project.

In the present book, the term condensation polymers is used as solely referring to the type of heterochain macromolecules regardless of the chemical mechanism and of the way of their preparation, *e.g.*, by means of additional polymerisation or condensation polymerisation (polycondensation). Although attention is focused mainly on transreactions, additional condensation is also discussed in some chapters since both types of reactions take place simultaneously, particularly under vacuum. Chemical reactions of the destructive type are beyond the scope of this book. It should be mentioned also that the good intention of the Editor to introduce more or less uniform terminology, in the description of the reactions under consideration, failed because the preference of one or another term for the same reaction, expressed by some authors, was too strong.

An international team of polymer chemists and physicists experienced in the field tried to cover the main topics related to the chemical interactions in condensation polymers. As Editor, I enjoyed the work with the individual contributors and gratefully appreciate their support, prompt response and patience. My thanks are also extended to the Institute for Structure of the Matter, Madrid, for the hospitality during my sabbatical tenure offered by DGICYT, Spain, where this project was finalised. I am greatly indebted to my coworker Mrs. S. Petrovich for her everyday help.

Madrid, Dezember 1998

S. Fakirov
Editor

SYMBOLS USED IN THIS BOOK

Symbol	Definition
a, b	initial molar fractions of polycondensates 1 and 2
A	absorbance
$[A]$	concentration of low molecular weight species
B	degree of randomness
B	term accounting for adsorption and other enthalpic processes in SEC column
c_{A}, c_{B}	molar fraction of comonomer A or B in copolymer
C_1	constant
ΔC_{p_i}	difference in specific heats between the liquid and glassy states of component i
d	spacing of crystal planes
d	diagonal length of indentation
$d_{(hkl)}$	spacing of (hkl) planes
D	polydispersity index
DP	degree of polymerisation
e_{HOM}	molar fraction of homopolymers
E	energy
E	elastic modulus
E'	storage modulus
E''	loss modulus
f	atomic scattering factor
$f_{\mathrm{A_iB_jA_k}}$	molar fraction of triad $\mathrm{A_iB_jA_k}$ with B_j as the central unit
f_{BB}, f_{BN}	molar fraction of BB or BN dyad
F	SEC mobile phase volume flow rate
F	force applied by indenter
F_{A_i}	molar fraction of structural unit A_i
$F_{\mathrm{A_iB_j}}$	molar fraction of an $\mathrm{A_iB}_j$ dyad in a polymer
$F_{jk}(Z)$	Fourier transform of cross-convolution of monomer j with monomer k
F_n	frequency of nucleus n
F_n	frequency of block length n
G	crystal growth; modified Avrami parameter for microhardness

Symbol	Definition
G''	loss modulus
$G(n_{\mathrm{cyc}})$	probability of formation of a polymer having n_{cyc} units
h	Planck's constant
H	microhardness
H	microhardness (or hardness) of crystallised sample
ΔH	transition enthalpy
ΔH	reaction heat
ΔH	enthalpy of melting
H_a	microhardness of quenched amorphous sample
$H_{a,i}$	microhardness of fully amorphous powder
H_c	enthalpy of crystallisation
H_c	hardness of crystals
ΔH_c	enthalpy of crystallisation
ΔH_f	molar heat of fusion
$H_i^{\max}$	microhardness of fully crystallised powder
H_{loc}	local magnetic field experienced by a nucleus
H_m	enthalpy of melting
H_m, H_M	microhardness of minor and major components of blend
$H^{\max}$	maximum microhardness
H_m°	melting enthalpy of a perfect infinite crystal
H^{BL}	microhardness of coreactive PC/PET blend
H^{PC}	microhardness of homo PC
ΔH_u	molar heat of melting of crystalline units A at T_m°
$\boldsymbol{H}_0$	static magnetic field
$\boldsymbol{H}_1$	rotating magnetic field orthogonal to $\boldsymbol{H}_0$
I	spin angular momentum quantum number
I_{A}, I_{AA}	signal intensity of A–A bond
$I_{\mathrm{A}'}$, I_{AB}	signal intensity of A–B bond
I_{B}, I_{BB}	signal intensity of B–B bond
$I(Z)$	scattering along chain axis direction
${}^xJ$	strength of scalar coupling between coupled nuclei with x intervening bonds
k	Boltzmann's constant
k	monomeric transesterification rate
k, k_{AB}	monomer ratio A/B in A–B copolymer
k_2	transreaction rate constant
k_n	reaction rate
K	equilibrium constant
K	geometrical factor
K	Mark–Houwink coefficient of PS standard
K_s	Mark–Houwink coefficient of sample
K_{SEC}	ratio of average solute concentration inside pores to that outside the pores (SEC)

Symbol	Definition
l_c	lamellar thickness
L	total number of units in sample
L	long period or spacing (SAXS measurements)
$\boldsymbol{L}$	torque
$\bar{L}_{\mathrm{A}}$	average length of block A
$\bar{L}_{nS}$	number-average sequence length of an S unit
$\bar{L}_{nT}$	number-average sequence length of a T unit
m	magnetic quantum number
m	average length of polymer unit, or aliphatic polymer unit
m	parameter describing internal mobility of groups in a single chain
M	molecular weight
M_{jk}	molar fraction of k in completely random copolymer of monomers j and k, modified for non-randomness if necessary
M_n	number-average molecular weight
$\bar{M}_n$	number-average molecular weight
M_w	weight-average molecular weight
$\bar{M}_w$	weight-average molecular weight
M_z	z-average molecular weight
n	repetition factor; $n(x+y)$ = degree of polymerisation
n	average degree of polymerisation at time t
n	average length of aromatic polymer unit
n	degree of polymerisation
n	number of ester linkages
n	Avrami exponent for microhardness
n_0	average degree of polymerisation at time 0
n_1, n_2	slopes of microhardness *vs.* time curves
(n_{A}), (n_{B})	number-average sequence lengths of comonomers A and B in copolymer
n_{cyc}	number of units in a cycle
N_+, N_-	population of upper and lower energy states
$N_{\mathrm{A}_m\mathrm{B}n}$	number of times an oligomer $\mathrm{A}_m\mathrm{B}_n$ appears in simulated sample
p	number of polymer reactive groups per unit volume
p	number of $\mathrm{A_1B_1}$ units on polyamide 46
p_∞	upper limit of p at infinite concentration
p_{AA}	probability of crystallisable homopolymer unit A being followed by another A unit
p_j	molar fraction of monomer j
P	probability of reaction at a given site
$P_{\mathrm{A}_i\mathrm{A}_j}$, $P_{\mathrm{A}_i\mathrm{B}_j}$	probability of A_i unit being followed by A_j unit, or B_j unit, in copolymer

Symbol	Definition
P_S	molar fraction of sebacate
P_{ST}	probability of finding a T unit next to an S unit
P_T	molar fraction of terephthalate
P_{xy}	element in probability matrix for sequence distribution of units x,y
q	number of A_2B_2 units in polyamide 46
Q_1	point at which exchange takes place
r	distance between nuclei
r	transcondensation ratio
r	cross reaction parameter
R	gas constant
s_A,s_B	molar fraction of comonomer A or B in sample (mixture of comonomers and copolymer)
S	number of exchange events per initial molecule
ΔS	reaction entropy
$\Delta S'$	entropy increase for randomisation of initial copolymer blend or diblock
$\Delta S''$	entropy increase for randomisation of restored block copolymer
t	extrusion time
t_1	evolution period
t_2	acquisition (detection) time
t_a	annealing time
t_c	crystallisation time
$t_{c_{1\to 2}}$	time at which hardening kinetics change
t_m	melt-pressing time
t_R	SEC peak elution time
T	temperature
T_1	spin–lattice relaxation time (longitudinal relaxation time)
T_2	spin–spin relaxation time (transverse relaxation time)
T_a	annealing temperature
T_b	Brill transition temperature
$T_{b,c}$	Brill transition temperature during cooling from the melt
T_c	crystallisation temperature
T_{cn}	crystal–nematic transition temperature
T_g	glass transition temperature
T_g^{BL}	glass transition temperature of coreactive PC/PET blend
T_{gi}	glass transition temperature of component i
T_g^{PC}	glass transition temperature of homo PC
T_h	healing temperature
T_m	melting point
T_m', T_m''	melting points of less and more perfect crystallites in randomised equimolar PET/PC copolymer, respectively

Symbol	Definition
T_m^*	equilibrium melting temperature of random copolymer
T_m°	equilibrium melting temperature of semicrystalline homopolymer
T_M°	thermodynamic equilibrium melting point
V_0	interstitial liquid volume between SEC packing particles
V_{cn}	crystal–nematic transition temperature
V_e	elution volume
V_i	internal pore volume (SEC)
V_k	vector in MOSES program
V_R	SEC elution (retention) volume
w	molar fraction of one coponent in copolyester blend
w, x, y, z	average lengths of polymer sequences
$\boldsymbol{w}$, $\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$	average lengths of polymer sequences
w_c	degree of crystallinity
w_{co}	weight fraction of co-oligomers
w_{HA}, w_{HB}	weight fraction of homopolymers A or B
w_i	mass fraction of component i
w_{PEN}	total concentration of PEN units
w_{PET}	concentration of PET units
W_i	weight fraction of component i
W_k	vector in MOSES program
W_n	probability of block length n
x	distance from chain ends
x	number-average sequence length of A_1B_1 groups
x	number of transesterification events
x, y	number-average sequence lengths of A_1B and A_2B
x, y	fractional contribution of x- or y-mer to molar volume of XY polymer
$\boldsymbol{x}$, $\boldsymbol{y}$	average lengths of ethylene terephthalate and bisphenol A terephthalate sequences
$x_{0,i}$	nominal concentration of starting material i
$x_{0,m}$	concentration of starting material m of minor nominal concentration
x_{A}	molar fraction of crystallisable units A
x_i	concentration of component i in blend
x_i	actual volume fraction of component i in blend
X	molar fraction of A_1B_2 or A_2B_1 dyads at time t
X_e	molar fraction of A_1B_2 or A_2B_1 dyads at equilibrium
X_i	molar fraction of component i
$Y_0(\mathrm{A})$, $Y_0(\mathrm{B})$	initial number-average degree of polymerisation of A or B
z	distance along chain axis; atomic coordinate along the chain axis direction
z_j	monomer j separation
Z	reciprocal space coordinate of z

Symbol	Definition
α	fraction of minor component m
α	Mark–Houwink coefficient of PS standard
α_L	linear crystallinity, l_c/L
α_s	Mark–Houwink coefficient of sample
γ	magnetogyric ratio
δ	chemical shift
δ^2	cohesive energy density
$\tan\delta$	loss factor
ε	strain
ε_0	initial number of chain ends
ε_b	relative elongation at break
η^*	viscosity
$[\eta]$	intrinsic viscosity
$\langle\eta^2\rangle$	invariant in Chapter 7, Eq. (15)
η_{int}	intrinsic viscosity
θ	angle between magnetic moment μ and applied field $\boldsymbol{H}_0$
2θ	scattering angle
λ	draw ratio
$\boldsymbol{\mu}$	magnetic moment
ν	frequency of energy quantum absorbed or emitted by nucleus
ν	number of transesterication events per monomer
ν_0	precessional or Larmor frequency
ρ_a	electron density of amorphous phase
ρ_c	electron density of crystalline phase
σ	screening constant
σ	normal stress
σ_b	stress at break
σ_e	fold surface free energy
φ	degree of crystallinity
χ	degree of randomness
Ψ	percentage of transamidation

Chapter 1

Interchange Reactions in Condensation Polymers and Their Analysis by NMR Spectroscopy

H. R. Kricheldorf, Z. Denchev

1. Introduction

Interchange reactions* are a phenomenon that concerns numerous classes of polymers. Recently, these interactions have been subject to extensive research due to the fact that they open the route to some new methods of polymer modification and even the preparation of novel polymer materials.

Interchange reactions take place at elevated temperatures (most frequently in the melt) between functional groups belonging to molecules with different degrees of polymerisation or different chemical compositions. As a rule, they are reversible equilibrium interactions, typical of polycondensates, and have been recognised since these polymers were first made. Most prominent examples are polyesters and polyamides, where interchange reactions are best studied and understood. However, during recent decades, a number of publications have dealt with interchange reactions that involve urethane and urea groups, Si–O bonds, *etc.*; these also deserve special attention.

*There is a great variety of different terms used in the literature when addressing the interchange reactions, *e.g.*, transreactions, transesterification, ester–ester interchange, *etc.* In this chapter, the general term "interchange reactions" is used consistently. It is classical English, widely accepted and highly versatile.

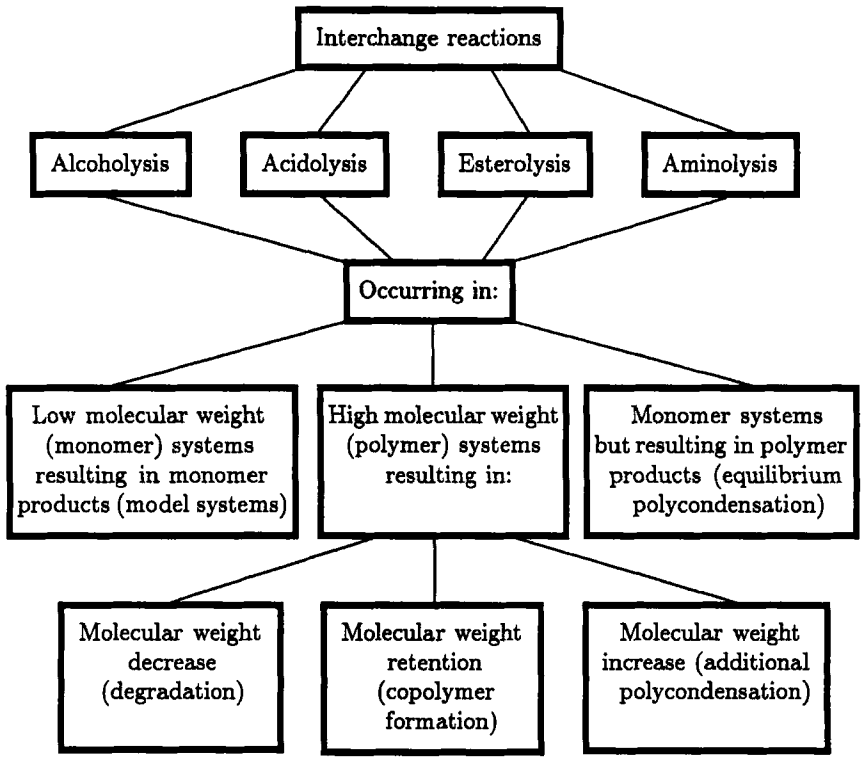

Figure 1. Relationships between interchange reactions

This chapter covers the characteristics of some significant types of interchange reactions, such as acidolysis, alcoholysis, aminolysis, esterolysis, taking place in low or high molecular weight systems and resulting in different products — low molecular weight compounds, homo- or copolymers. The scheme in Figure 1 depicts the mutual connections and relations between all the types of interchange reaction. However, this classification is quite superficial: for instance, when discussing the interchange reactions in polymer systems, attention is focused on copolymer formation, although it is clear that, depending on the conditions of treatment and chemical composition of the blend constituents, the process should be accompanied by either degradation or additional polycondensation. These three processes are closely connected and should be considered as inevitable parts of the condensation equilibrium.

It is worth noting that there had been some indications that interchange reactions might be possible in some carbochain polymers (*i.e.*, with all-carbon backbones). These also result in polymer modification, but occur to a much lesser degree. For this reason they are treated as secondary

reactions, taking place during the polyaddition [1,2], and are beyond the scope of this chapter.

Very often it is of prime importance to discover the effect of the interchange reactions on the microstructure of the respective system — for instance, to find out whether or not a copolymer is formed as a result of interchange reactions in monomer or polymer systems, or to determine the sequence length distribution, *etc.* High resolution nuclear magnetic resonance (NMR) has proved to be the most useful method for the direct experimental determination of the polymer microstructure. Of the two nuclei ^{1}H and ^{13}C, which possess spin and are common in synthetic polymers, ^{1}H initially served as the spin probe in NMR polymer studies. However, though ^{1}H is more abundant than ^{13}C, proton NMR spectra of synthetic polymers suffer from a narrow dispersion of chemical shifts and extensive ^{1}H–^{1}H spin coupling. ^{13}C NMR, as currently practiced, does not suffer from these difficulties, of which the latter has recently been turned to advantage for ^{1}H NMR by 2D techniques. The advent of proton-decoupled spectra recorded in Fourier-transform mode has quickly made ^{13}C NMR spectroscopy the method of choice for determining polymer microstructures. Other methods, such as ^{15}N and ^{29}Si NMR, are rapidly gaining importance as irreplaceable tools for the characterisation of siloxanes and N-containing polycondensates. For all these reasons, the basic principles and importance of modern NMR techniques in view of their application for interchange reaction characterisation are discussed in this chapter.

2. Nuclear magnetic resonance as an analytical tool (^{1}H, ^{13}C, ^{15}N and ^{29}Si NMR)

2.1. *Basics of the method*

NMR spectroscopy belongs among the radiospectroscopic methods, where the basic transitions are those between spin (or magnetic) energy levels of the nuclei. In contrast to the optical transitions (*e.g.*, vibrational, rotational, electronic), the nucleus can absorb radiofrequencies only if the molecules are placed in a strong, external magnetic field. This is because in the absence of magnetic field, the different spin states of the nuclei have the same energy, *i.e.*, they are degenerate.

2.1.1. *Magnetic properties of the nucleus*

While the nuclei of all atoms possess charge and mass, not every nucleus has angular momentum and a magnetic moment. Nuclei with odd mass numbers have spin angular momentum quantum numbers I, with values that are odd-integral multiples of 1/2. Nuclei with even mass numbers are spinless if their nuclear charge is even, and have integral spin I if their nuclear charge is odd.

The angular momentum of a nucleus with spin I is simply $I(h/2\pi)$, where h is Planck's constant. If $I \neq 0$, the nucleus will possess a magnetic moment, μ, which is taken parallel to the angular-momentum vector. A set of magnetic quantum numbers m, given by the series

$$m = I, I-1, I-2, \ldots, -I \tag{1}$$

describes the values of the magnetic moment vector which are permitted along any chosen axis. For nuclei of interest here (^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P), $I = 1/2$, and thus $m = +1/2$ and $-1/2$. In general, there are $2I + 1$ possible orientations of $\boldsymbol{\mu}$, or magnetic states of the nucleus. The ratio of the magnetic moment and the angular momentum is called the magnetogyric ratio, γ:

$$\gamma = 2\pi\mu/hI \tag{2}$$

and is characteristic of a given nucleus.

The nuclei commonly observed in NMR studies of polymers usually have spin $I = 1/2$, and are characterised by $2I + 1 = 2$ magnetic states, $m = +1/2$ and $-1/2$. Both nuclear magnetic states have the same energy in the absence of a magnetic field, but they correspond to states of different potential energy upon application of a uniform magnetic field $\boldsymbol{H}_0$. The magnetic moment μ is either aligned along ($m = +1/2$) or against ($m = -1/2$) the field $\boldsymbol{H}_0$, with the latter state corresponding to a higher energy. Detection of the transitions of the magnetic nuclei between these spin states [$m = +1/2$ (parallel), $m = -1/2$ (antiparallel)] are made possible by the NMR phenomenon.

Table 1. Magnetic characteristics of some atomic nuclei [3]

Nucleus	Natural abundance (%)	Atomic number I	Magnetogyric ratio γ (rad.s.Oe)	Magnetic moment μ (magnetons)	Quadropole moment Q (10^{-24} cm^2)	Relative amplitude of the signal	Resonance frequency (MHz)
$^{1}H^{1}$	99.98	1/2	26753	2.79270	—	1.000	100
$^{2}H^{1}$(D)	0.016	1	4107	0.85738	0.00274	0.010	15.4
$^{11}B^{5}$	81.17	3/2	8583	2.6880	0.0355	0.165	32.2
$^{12}C^{6}$	98.89	0	—	—	—	—	—
$^{13}C^{6}$	1.11	1/2	6728	0.70216	—	0.016	25.1
$^{14}N^{7}$	99.64	1	1934	0.40357	0.02	0.001	7.2
$^{15}N^{7}$	0.36	1/2	−2712	−0.28304	—	0.001	10.1
$^{16}O^{8}$	99.76	0	—	—	—	—	—
$^{17}O^{8}$	0.037	5/2	−3628	−1.8930	−0.004	0.029	13.5
$^{19}F^{9}$	100	1/2	25179	2.6278	—	0.834	94.0
$^{28}Si^{14}$	92.28	0	—	—	—	—	—
$^{29}Si^{14}$	4.67	1/2	−5319	−0.55477	—	0.078	19.9
$^{31}P^{15}$	100	1/2	10840	1.1305	—	0.066	40.5
$^{32}S^{16}$	95.06	0	—	—	—	—	—
$^{33}S^{16}$	0.74	3/2	2054	0.64274	−0.064	0.002	7.67