



*JOURNAL OF CHROMATOGRAPHY
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*polymer
characterization
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chromatography*

G. Glöckner

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Polymer Characterization by Liquid Chromatography

Gottfried Glöckner
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ELSEVIER
Amsterdam — Oxford — New York — Tokyo 1987

This book is the revised translation of

Polymercharakterisierung durch Flüssigkeitschromatographie

published by VEB Deutscher Verlag der Wissenschaften, Berlin, DDR, 1980

Translated by Bernhardt Simon, Berlin, DDR

Published in coedition with VEB Deutscher Verlag der Wissenschaften, Berlin

Elsevier Science Publishers

Sara Burgerhartstraat 25

P. O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the U.S.A. and Canada

Elsevier Science Publishing Company

52 Vanderbilt Avenue

New York, NY 10017

Library of Congress Cataloging-in-Publication Data

Glöckner, Gottfried, 1925—

Polymer characterization by liquid chromatography.

(Journal of chromatography library; v. 34)

"Revised translation of Polymercharakterisierung
durch Flüssigkeitschromatographie . . . 1980" — T.p. verso.

Bibliography: p.

Includes index.

1. Polymers and polymerization—Analysis. 2. Liquid chromatography. I. Title. II. Series.

QD139.P6G5613 1986 547.7'046 86-6237

ISBN 0-444-99507-2

ISBN 0-444-99507-2 (Vol. 34)

ISBN 0-444-41616-1 (Series)

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Printed in the German Democratic Republic

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Preface

The main subject of this book is the characterization of plastics. To a high degree the properties of these polymers depend on the distribution of the molar mass and of other structural features. Small contributions frequently have a great effect. The characterization of polymers cannot be restricted to the determination of mean values but must yield information on these distributions. Using classical methods, the analytical fractionation of polymer homologues and structurally isomeric polymers is extremely time-consuming. Therefore efficient chromatographic techniques are being increasingly employed in modern polymer characterization.

In the first place, HPLC is applied in the form of size exclusion chromatography (gel permeation chromatography), but it is also possible to use other separation mechanisms. In this volume, more space is devoted to these possibilities than is merited by their current range of application, since the author believes that many a problem of characterization that still exists, besides the determination of the molar mass distribution, will be solved by separation techniques of the non-exclusion types. Nevertheless, the relative importance of size exclusion chromatography will not only be preserved but may even increase because of its use to complement other chromatographic techniques.

The first part of this book is intended as an introduction. For the polymer chemist, these chapters are meant to serve as an aid to the understanding of chromatography; moreover they provide the chromatographer, whose work is extending to the separation of macromolecules, with necessary information about polymers. So the book does not presuppose specialist knowledge and can guide the reader in the challenging borderline area between polymer science and chromatography. For scientists involved in practical work the most important parts are probably sections C "Chromatography under real conditions" and D "Applications".

As already mentioned, size exclusion chromatography (SEC) is without doubt the most common, and therefore also the most important, form of chromatographic polymer characterization. Many explanations, especially when dealing with the experimental characteristics of elution chromatography, are of importance for SEC, and also relevant to adsorption and partition techniques. To avoid repetition, an arrangement was chosen which permits a complete picture of macromolecular chromatography, from the principles to the applications. In this way it was possible to avoid splitting the book into separate parts such as "Exclusion chromatography", "Adsorption chromatography" and "Partition chromatography". At the same time it was possible to present the whole complex of chromatographic mechanisms without difficulty. This order also made it possible to place certain fundamental explanations, for example of the gradient technique or kinetic band broadening, according to their priority. Admittedly this order could cause difficulties for a reader only interest-

ed in one particular chromatographic method, because he will not find all the relevant information in successive chapters. However, notes in the text and the index should help in finding any item without too much difficulty.

The manuscript was aimed at helping the analyst or polymer chemist who is looking for information about chromatographic methods for the characterization of polymers. I therefore consciously tried to present the material in the most straightforward way possible. I have also tried to simplify the symbolism as far as possible. Since it is not possible simply to mix the different sets of symbols from chromatography on the one hand and polymer science on the other, because they overlap to some extent, in some cases I have had to deviate from the norm.

The German edition of this book, "Polymercharakterisierung durch Flüssigkeitschromatographie", was published by VEB Deutscher Verlag der Wissenschaften, Berlin, in 1980, and included references to original papers published up to 1977. In places the text has undergone considerable modification as compared with the 1980 edition.

The second part of the book, "Concepts of chromatography: mechanisms and materials", underwent many changes from the German edition. In the present book the packing materials are no longer discussed in connection with an individual separation process, because of the ever-increasing number of materials available which, depending on the conditions, can show separating efficiency due to quite different mechanisms. A well-known example of this is silica.

Chapters 10—12 have been completely rewritten and aim to show a more rounded picture of materials used in liquid chromatography. New sections deal with support characterization, bonded phases and cross-linked organic materials.

However, the increase in length due to these additions made it necessary to omit whole chapters of the German edition. Thus, the description of the apparatus for elution chromatography, of the historical development of chromatographic methods and several other passages have been deleted.

It soon became clear just how difficult it was to translate such a greatly revised manuscript. The fact that the revision, translation and editing of the manuscript had to be carried out more or less simultaneously added further difficulties. I wish to thank all those who have contributed to the preparation of this book for their cooperation, not least Fräulein MIEDLICH of the Department of Chemistry of VEB Deutscher Verlag der Wissenschaften, who did a great deal of the detailed editorial work with untiring patience, and her department head, Dr. FICHTE, who had to conduct the difficult concert.

In preparing the revised edition, several thousand new papers were taken into consideration. I would like to thank all colleagues who sent me offprints of their interesting work. I am also grateful for the valuable help received from the library staff and from other departments of the Technical University of Dresden. My special thanks go to Frau CHARLOTTE MEISSNER, who again helped me most conscientiously to cope with the wealth of literature. She also showed remarkable patience in preparing about 800 new entries for the list of references. Dr. ZIMMERMANN, with great enthusiasm, then guaranteed that the advantages of electronic data processing could be utilized in indexing these data.

Now it is for the reader to decide whether he can really benefit from these efforts. Critical comments will be gratefully received.

GOTTFRIED GLÖCKNER

Table of contents

	Glossary of symbols and abbreviations	17
A	Basic facts	23
1.	Introduction	23
2.	Chromatographic techniques	27
3.	Foundations and fundamental concepts of chromatography	31
3.1	Retention time, mobile phase hold-up time, and relative rate of migration	31
3.2.	Distribution constants	32
3.3.	The formation of bands	33
3.4.	Chromatographic resolution	39
3.5.	Separation of multicomponent mixtures	41
3.6.	Non-linear concentration relationships	43
4.	Macromolecules: size, constitution, configuration, conformation	45
4.1.	Molar mass and degree of polymerization	45
4.2.	Distribution of the degrees of polymerization	46
4.2.1.	Mean values	46
4.2.2.	Frequency and mass distribution functions	48
4.2.3.	Determination of the distribution from fractionation data	49
4.2.4.	Theoretical functions for the distribution of degrees of polymerization	49
4.2.4.1.	The generalized Schulz distribution	50
4.2.4.2.	Additional functions for the description of the chain length distribution	51
4.3.	Constitution of the macromolecules	53
4.4.	Configuration of the macromolecules	55
4.5.	Conformation of the molecules	56
4.6.	Associates	58
5.	Interactions between polymers and solvents	59
5.1.	Solubility parameters	59
5.2.	Thermodynamic quality of a solvent	62
5.3.	Polymers in single solvents	65
5.3.1.	Phase equilibria in binary systems	65
5.3.2.	Phase equilibrium for polymolecular samples in a single solvent	67
5.4.	Polymers in mixed solvents	70
5.4.1.	Selective solvation	70
5.4.2.	Solvent segregation during precipitation	71
5.4.3.	Characterization of polymers on the basis of solubility differences	72
5.5.	Resorption and desorption of a solvent	72

6.	Adsorption of polymers	74
6.1.	Experimental methods and results	75
6.1.1.	Adsorption isotherms	75
6.1.2.	Viscosimetric investigations	76
6.1.3.	Ellipsometry	77
6.1.4.	Electrosorption analysis	79
6.1.5.	IR spectroscopy	79
6.1.6.	Electron spin resonance (ESR)	80
6.1.7.	Calorimetry	82
6.1.8.	Magnetic birefringence	82
6.2.	Discussion of the experimental results	83
6.2.1.	The structure of the adsorption layer	83
6.2.2.	Effect of the temperature	86
6.2.3.	Effect of the solvent	87
6.2.4.	Effect of the molecular size	87
6.2.5.	Effect of the surface structure	90
6.3.	A concluding comparison	92
B	Concepts of chromatography : mechanisms and materials	93
7.	Adsorption chromatography	93
7.1.	Adsorption equilibrium (competition model)	93
7.2.	Discussion of eqn. (7-11) for adsorption chromatography on polar adsorbents	95
7.3.	Experimental evaluation of the parameters	99
7.4.	The rôle of the eluent	102
7.4.1.	Eluent mixtures	102
7.4.2.	Eluent demixing	104
7.5.	Secondary effects	105
7.5.1.	Interactions in a solution	105
7.5.2.	Effects of the adsorbate structure	106
7.5.3.	Localized adsorption	106
7.6.	The rôle of the eluent in reversed-phase chromatography	107
7.7.	The rôle of solubility parameters in chromatographic processes	111
7.8.	Other approaches to solvent behaviour in liquid chromatography	113
7.9.	Resolution in adsorption chromatography	115
8.	Separation by size exclusion	116
8.1.	Distribution equilibrium in SEC	116
8.2.	Relationship between the molar mass and the elution volume	118
8.3.	Universal calibration of gel chromatography	121
8.3.1.	The Q value concept	121
8.3.2.	Universal calibration by means of the hydrodynamic volume	121
8.3.3.	Calibration by samples with broad distributions	127
8.3.4.	Normalized calibration curves	130
8.4.	Non-linear calibration relationships	131
8.5.	The principle of separation	132
8.6.	Resolving power of SEC	135
9.	Chromatographic separation by partition	138
9.1.	Liquid-liquid partition of low-molecular-weight samples	138
9.2.	Liquid-liquid partition of macromolecular samples	139
9.2.1.	Fractionation of polymers by partition between immiscible liquids	139
9.2.2.	Counter-current fractionation using an auxiliary polymer	140
9.3.	Counter-current chromatography	140

9.4.	Chromatography on bonded phases	142
9.4.1.	Low-molecular-weight samples	142
9.4.2.	Macromolecular samples	143
9.5.	Precipitation chromatography	146
9.5.1.	Chromatographic sol-gel fractionation without a temperature gradient	147
9.5.2.	Chromatographic sol-gel fractionation with a temperature gradient	148
9.6.	Resolution of partition chromatography	152
9.7.	Supercritical fluid chromatography (SFC)	161
10.	Support materials	166
10.1.	Chemical aspects	167
10.2.	Shape and constitution of porous supports	170
10.3.	Classification by sizes	171
10.4.	Characterization of the pore system	173
10.4.1.	Specific surface area	173
10.4.2.	Pore volume	174
10.4.3.	Pore geometry	174
10.4.4.	Porosity	176
10.5.	Selection and characterization of the chromatographic activity	177
11.	Inorganic supports	181
11.1.	Silica gel	181
11.2.	High-disperse silicic acid, Aerosil®	187
11.3.	Alumina	187
11.4.	Magnesia	189
11.5.	Magnesium silicate (Florisil®, Magnesol®)	190
11.6.	Kieselguhr (diatomaceous earth)	190
11.7.	Carbon materials	190
11.8.	Porous glass	191
11.9.	Materials for precipitation chromatography	193
11.10.	Supports with a chemically modified surface (bonded phases)	194
11.10.1.	Preparation of chemically fixed coatings	195
11.10.2.	Properties	198
11.10.3.	Polymer layers on inorganic support particles	204
12.	Organic supports	207
12.1.	Cross-linked copolymers	207
12.1.1.	Cross-linked polystyrene	212
12.1.2.	Cross-linked polyvinyl acetate	215
12.1.3.	Methacrylate gels	217
12.1.4.	Cross-linked polyacrylamide	219
12.1.5.	Cross-linked polyacryloylmorpholine	221
12.1.6.	TSK Gel PW	222
12.2.	Separating materials based on natural macromolecules	223
12.2.1.	Cross-linked dextran	223
12.2.2.	Agarose gels	227
12.2.3.	Support materials based on cellulose	232
13.	Other mechanisms of separation	233
13.1.	Field-flow fractionation	233
13.2.	Hydrodynamic chromatography	238
13.3.	Membrane chromatography	239
13.4.	Foam fractionation	240

C	Chromatography under real conditions	241
14.	Gradient technique	241
14.1.	Definitions and systematics	241
14.1.1.	Orientation of the gradient	241
14.1.2.	Form of the gradient	242
14.1.3.	Gradient-analogous variations	243
14.2.	Objectives of gradient chromatography	244
14.3.	Survey of gradient types	245
14.4.	Resolving power of the gradient technique	250
15.	The influence of kinetic factors	258
15.1.	Band broadening due to axial diffusion	259
15.2.	Band broadening due to flow effects	260
15.2.1.	Eddy diffusion	260
15.2.2.	Substance displacement in the flowing phase	261
15.3.	Band broadening due to resistance to mass transfer	261
15.3.1.	Diffusion into the interior of the stationary phase	262
15.3.2.	Diffusion in the stagnant mobile phase	263
15.3.3.	Retarded establishment of equilibrium at the phase boundary	263
15.3.4.	Combination of the retardation contributions	264
15.4.	Interaction of all kinetic factors	264
15.5.	Conclusions drawn from the theory	269
16.	Special problems	275
16.1.	Determination of the molar mass distribution from a chromatogram	275
16.1.1.	Solution of eqn. (16-2) by minimization methods	279
16.1.2.	Solution of eqn. (16-2) by iteration	280
16.1.3.	Solution of eqn. (16-2) after approximating it by a polynomial	282
16.1.4.	Solution of eqn. (16-2) by Fourier transformation	283
16.1.5.	Solution of an equivalent partial differential equation instead of eqn. (16-2)	284
16.1.6.	Correction by the subtraction of ideal distributions	284
16.2.	Determination of the mean values of the molar masses	285
16.3.	The dispersion function $G(v - \gamma)$	286
16.3.1.	Symmetric and asymmetric distributions	286
16.3.2.	Determination of the parameters μ_2 , μ_3 and μ_4	288
16.4.	Effect of dispersion on the calibration curve	297
16.5.	Characterization of the separation efficiency in the chromatography of polymers	299
16.5.1.	Reproducibility	299
16.5.2.	Characterization by the height equivalent to a theoretical plate	300
16.5.3.	Resolution, specific resolution, resolution index and separation power	302
16.5.4.	Accuracy of molar mass values calculated from SEC curves	304
16.6.	Real GPC	304
16.6.1.	Adsorption and exclusion	307
16.6.2.	Solvophobic interactions in GPC	314
16.6.3.	Partition in the wall material	316
16.6.4.	Reduction of the available pore volume by solvent adsorption	320
16.6.5.	Electrostatic repulsion	322
16.6.6.	Combination of adsorption, partition and exclusion	323
16.7.	Experimental determination of the volume portions in LC columns	326
16.8.	Degradation by shear	328
16.9.	Energy aspects	328
17.	Techniques in macromolecular elution chromatography	330
17.1.	Packing of HPLC columns	330
17.1.1.	Preparation of the columns	330

17.1.2.	Dry packing	330
17.1.3.	Wet packing technique	331
17.1.3.1.	Gels	331
17.1.3.2.	Non-swelling packing materials	332
17.1.4.	Final manipulations	335
17.2.	Flow resistance	335
17.3.	Exchange of columns	338
17.4.	The service life of a column	338
17.5.	Sample introduction	339
17.6.	Stopped-flow technique	341
17.7.	High-precision measurements of the elution volume	341
17.8.	Recycling	344
17.9.	Elution chromatography on a preparative scale	348
17.9.1.	Preparative SEC	349
17.9.2.	Preparative precipitation chromatography	352
17.9.3.	Continuous preparative chromatography	353
17.9.4.	Comparisons and conclusions	355
D	Applications	357
18.	Adsorption chromatography of polymers — experimental parameters and results	357
18.1.	Rate of adsorption	357
18.2.	Desorption behaviour	360
18.3.	Conclusions for adsorption chromatography	362
19.	Experimental parameters and results of size exclusion chromatography	377
19.1.	Influence of the sample size	377
19.2.	Working temperature	386
19.3.	Solvents	386
19.3.1.	Exclusion chromatography with solvent mixtures	387
19.3.2.	Addition of salts to organic eluents	389
19.3.3.	Size exclusion chromatography of aqueous solutions	394
19.3.3.1.	Ion exclusion	395
19.3.3.2.	Ion inclusion	399
19.3.3.3.	Polyelectrolyte swelling	400
19.3.3.4.	Adsorption and hydrophobic interactions	401
19.3.3.5.	The calibration of aqueous exclusion chromatography	404
19.4.	SEC investigations on band broadening	405
19.5.	High-speed SEC	407
19.6.	Reliability of the results	412
19.6.1.	Round robin testings	412
19.6.2.	A working technique	413
19.6.3.	Size exclusion chromatography with long columns	426
19.6.4.	Micro SEC	427
19.7.	Size exclusion chromatography of copolymers	428
19.7.1.	Molar mass distribution (MMD) and chemical composition distribution (CCD)	429
19.7.2.	Practical examples	431
19.7.3.	Determination of the chemical composition	434
19.7.3.1.	UV detection	434
19.7.3.2.	IR detection	434
19.7.3.3.	Microchemical analysis	435
19.7.3.4.	Automatic turbidimetric titration of SEC eluates	436
19.7.3.5.	Combination of chromatographic techniques	437
19.8.	SEC of polymers with long-chain branching	440
19.8.1.	The relationship between g' , g and the number, b , of branch points per molecule	440

19.8.2.	Universal calibration for branched polymers	443
19.8.3.	Evaluation of the elugrams of branched polymers	444
19.8.3.1.	The Drott-Mendelson method	444
19.8.3.2.	The method by Ram and Miltz	445
19.8.3.3.	Branching analysis with a viscosity detector	445
19.8.3.4.	Branching analysis with a light-scattering detector	447
19.8.4.	Branching analysis by a combined investigation by SEC and an ultracentrifuge	449
19.8.5.	Branching analysis including the preparative fractionation of the sample	450
19.9.	Special forms of size exclusion chromatography	452
19.9.1.	Vacancy chromatography	452
19.9.2.	Column scanning	453
19.10.	Particle chromatography	453
19.11.	Gel permeation chromatography of small molecules and oligomers	459
19.11.1.	The relationship between the size of small molecules and their elution volume	460
19.11.2.	Non-exclusion effects in the GPC of small molecules	461
19.11.3.	Baseline separation of oligomers	464
20.	Experimental parameters and results of precipitation chromatography	467
20.1.	Time required for an analysis	467
20.2.	Methodical preparatory work for the determination of the separation conditions	474
20.3.	Prognosis	475
21.	Thin-layer chromatography	476
21.1.	Flow parameter and speed of migration	476
21.2.	The R_f value	478
21.3.	Elimination of activity effects	481
21.3.1.	The R_k value	481
21.3.2.	The vain attempt with the "relative R_f values"	482
21.3.3.	The R_f correction using two reference substances	483
21.4.	Special problems in thin-layer chromatography	484
21.4.1.	Spontaneous gradients	484
21.4.2.	Separating mechanisms	486
21.4.3.	Spot shapes	487
21.5.	Results of the TLC of polymers	489
21.5.1.	Thin-layer exclusion chromatography	489
21.5.2.	Thin-layer adsorption chromatography	495
21.5.2.1.	Separation by composition	495
21.5.2.2.	Separation according to the polymer architecture	495
21.5.2.3.	Separation according to the degree of polymerization	496
21.5.3.	Precipitation TLC	497
21.6.	Generation of gradients	499
21.7.	Quantitative evaluation	501
21.7.1.	Quantitative evaluation after staining	503
21.7.2.	Quantitative TLC evaluation by UV scanning	504
21.7.3.	Quantitative analysis after removal from the layer	505
21.7.4.	Substance immobilization at the start	505
21.8.	Importance of the thin-layer chromatography of polymers	507
	Bibliography	508
	Sources	566
	Subject index	568

Glossary of symbols and abbreviations

Minor symbols which are used only once are not included.

Glossary of symbols

<i>Symbol</i>	<i>Definition</i>	<i>Units</i>
1A	Surface area per gram of adsorbent	$\text{m}^2 \cdot \text{g}^{-1}$
A_2	Second virial coefficient	$\text{cm}^3 \cdot \text{g}^{-2} \cdot \text{mole}$
A_s	Surface area required by an adsorbed molecule	
a	Exponent for the Mark-Houwink relation, $[\eta] = K_\eta \cdot M^a$	
a_1	Activity (of component I in the mixture)	
a_i	Increment of A_s due to the structural element i of a molecule (Section 7.2.)	
b	Number of long chain branches per molecule	
b	Slope of gradient (Section 14.4.)	
b_0	Length of a statistical chain element	
C_1, C_2	Constants in SEC calibration, $V_e = C_1 - C_2 \log M$	
c	Solute concentration	$\text{g} \cdot \text{l}^{-1}$
c_0	Concentration of sample solution, starting concentration	
c_{eq}	Concentration of solution in adsorption equilibrium	
D	Linear diffusion constant	$\text{cm}^2 \cdot \text{s}^{-1}$
D	Dielectric constant	
D_1, D_2	Constants in SEC calibration, $M = D_1 \cdot e^{-D_2 \cdot V_e}$	
d	Diameter	
d_c	Internal diameter of the column	mm
d_o	Pore diameter	nm
d_p	Particle diameter of the packing	μm
d_a	Thickness of adsorption layer	nm
d_f	Film thickness of the stationary phase	
d_h	Thickness of the hydrodynamically effective layer	nm
ΔE_λ	Extinction of the solute at wavelength λ	
$F(v)$	Experimental SEC elution curve	
ΔG	Difference in standard free energy	
G_m	Band compression factor in gradient technique	
$G(v - y)$	Instrumental dispersion function	
g	Branching parameter, radius of gyration ratio, $g = \langle S^2 \rangle_{0, \text{br}} / \langle S^2 \rangle_{0, 1}$	
g'	Branching parameter, intrinsic viscosity ratio, $g' = [\eta]_{\text{br}} / [\eta]_1$	

H	Heterogeneity (dispersity) of a polymer sample, $H = \bar{M}_w/\bar{M}_n$	
ΔH	Enthalpy difference	
$H(M)$	Molar mass distribution (weight distribution function)	
$H(P)$	Chain length distribution	
$h(M)$	Molar mass frequency distribution	
$h(P)$	Chain length frequency distribution	
h	Plate height, height equivalent to a theoretical plate	μm
h_{eff}	Effective plate height	
h^*	Reduced plate height, $h^* = h/d_p$	
h_M	Plate height as determined with a probe polymer of molar mass M	
h_f	Plate height from the front part of a skewed peak	
h_r	Plate height from the rear part of a skewed peak	
h'_a	Longitudinal-diffusion plate height	
h'_e	Eddy-diffusion plate height	
h'_s	Plate height due to stagnant mobile phase	
h'_i	Plate height due to interparticle mobile phase effects	
h''_d	Plate-height contribution caused by resistance to mass transfer	
h''_f	Plate-height contribution due to diffusion in the stationary film	
h''_p	Plate-height contribution due to pore diffusion	
I	Ionic strength	
$I(M)$	Weight-cumulative distribution of molar mass	
K	Distribution constant (activity ratio), $K = a''_s/a'_s$	
K^+	Conventional distribution constant (concentration ratio), $K^+ = c''_s/c'_s$	
K^*	Adsorption constant, $K^* = K \cdot V_s$	$\text{cm}^3 \cdot \text{g}^{-1}$
K_{av}	Laurent-Killander distribution constant	
K_η	Constant factor in the Mark-Houwink relation, $[\eta] = K_\eta \cdot M^a$	
k	(Column) Capacity factor, mass distribution ratio, $k = m''_s/m'_s = K \cdot q = (t_e - t')/t'$	
k	Degree of coupling (SCHULZ MMD, Section 4.2.4.1.)	
k	Reaction rate constant	
L	Column length, length of separating path	m
L_M	Contour length of a chain molecule, $L_M = P \cdot l_{\text{eff}} = Z \cdot b_0$	
l_0	Bond length (for C—C: 154 pm or 1.54 Å units)	
l_{eff}	Effective length of the repeat unit of a chain	
M	Molar mass	$\text{g} \cdot \text{mole}^{-1}$
M_0	Molar mass of the repeat unit	
M_b	Molar mass of the chain portion between two neighbouring branch points	
M_{lim}	Exclusion limit of SEC column or separating material	
$M_{(t)}$	True molar mass value	
$M_{(w)}$	Molar mass value calculated from an uncorrected chromatogram	
\bar{M}_n	Number-average molar mass	
\bar{M}_v	Viscosity-average molar mass	
\bar{M}_w	Mass-average molar mass	
\bar{M}_z	z-Average molar mass	
m_0	Mass of the sample injected	$\text{g (mg, } \mu\text{g)}$
m_1	Mass of component I in a mixture	

m_a	Mass of adsorbed solute per gram of adsorbent	$\text{mg} \cdot \text{g}^{-1}$
N	Plate number, column plate count	
N_{eff}	Effective plate number, $N_{\text{eff}} = N \cdot Q^2$	
N_L	Avogadro's number, $N_L = 6.022 \cdot 10^{23}$	mole^{-1}
n	Number of moles	
Δn	Refractive index difference due to the solute	
n_p	Peak capacity, maximum number of peaks detectable in a chromatogram	
P	Degree of polymerization	
$\bar{P}_n, \bar{P}_v, \bar{P}_w, \bar{P}_z$	Average values, see molar-mass averages	
p	Pressure	MPa (kPa)
p_{CO}	Fraction of CO groups adsorbed (from IR measurements)	
p_{ESR}	Fraction of segments adsorbed (fixed, from ESR measurements)	
Q	Q Factor, molar mass per unit chain length	$\text{g} \cdot \text{mole}^{-1} \cdot \text{\AA}$
Q	Retention factor, capacity term for the resolution equation, $Q = k_i/(1 + k_1)$	
Q_i	Increment of adsorption energy due to the structural element i	
q	Phase ratio, ratio of stationary phase volume to mobile phase volume, $q_{\text{SEC}} = V_p/V_m$, in AC and LLC: $q_{\text{LC}} = V''/V_M$	
R	Gas constant	
R	Retention ratio, $R = t'/(t' + t'')$	
$\langle R^2 \rangle$	End-to-end displacement (mean-square value)	cm^2
R_M	Logarithmic function of retention rate, logarithmic capacity factor, $R_M = \log k = \log [(1 - R)/R]$	
R_f	Relative distance of migration in TLC, $R_f = s/L$	
R_s	Resolution	
R_{sp}	Specific resolution	
$R_{\theta, i}$	Rayleigh factor in light scattering	
RI	Resolution index	
r	Radius	
r_o	Pore radius	nm
r_p	Particle radius	μm
r_v	Rate of vaporization	
S	Selectivity factor in SEC, $S = (V_{e, II} - V_{e, I})/\log (M_I/M_{II})$	
S	Slope factor in gradient elution, $S = \log (k_w/k_i)/\varphi_{II}$	
ΔS	Entropy difference	
$\langle S^2 \rangle$	Mean-square radius of gyration	cm^2
S^0	Adsorption energy for the solute in adsorption from a pentane solution onto an adsorbent with standard activity $\alpha_A = 1$	
s	Distance travelled, migration distance of a solute	
sk	Skew parameter, molar-mass correction factor for band-broadening asymmetry	
T	Temperature	K
T	Separation power of SEC	
t	Time	
t'	Observed elution time of a non-retained substance	
t''	Net retention time	
t_M	Eluent hold-up time	
t_e	Total retention time, $t_e = t' + t''$	