

CRC  
Handbook of

# Enthalpy Data of Polymer-Solvent Systems

Christian Wohlfarth



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## PREFACE

Knowledge of thermodynamic data of polymer solutions is a necessity for industrial and laboratory processes. Furthermore, such data serve as essential tools for understanding the physical behavior of polymer solutions, for studying intermolecular interactions, and for gaining insights into the molecular nature of mixtures. They also provide the necessary basis for any developments of theoretical thermodynamic models. Scientists and engineers in academic and industrial research need such data and will benefit from a careful collection of existing data. However, no data books or databases detailing enthalpy changes in polymer solutions presently exist. Thus, the *CRC Handbook of Enthalpy Data of Polymer-Solvent Systems* builds a completely new and reliable collection of enthalpy data for polymer solutions from the original literature. It will be a very useful completion to the *CRC Handbook of Thermodynamic Data of Copolymer Solutions*, the *CRC Handbook of Thermodynamic Data of Aqueous Polymer Solutions*, and the *CRC Handbook of Thermodynamic Data of Polymer Solutions at Elevated Pressures* as these contain only a small amount of enthalpic data in comparison to all available data provided in this book.

The book is divided into six chapters: (1) Introduction, (2) Enthalpies of mixing or intermediary enthalpies of dilution, (3) Polymer partial enthalpies of mixing at infinite dilution or polymer first integral enthalpies of solution, (4) Solvent partial enthalpies of mixing measured by calorimetry, (5) Partial molar enthalpies of mixing or solution of solvents in molten polymers from inverse gas-liquid chromatography (IGC), and (6) Table of additional information on enthalpy effects. Finally, appendices quickly route the user to the desired data sets. Thus, the book covers all the necessary areas for researchers and engineers who work in this field.

In comparison with low-molecular systems, the amount of data for polymer solutions is still rather small. About 800 literature sources were perused for the purpose of this book, including some dissertations and diploma papers. About 1770 data sets, i.e., 620 data sets on enthalpies of mixing or intermediary enthalpies of dilution, 970 data sets for polymer partial enthalpies of mixing or solution at infinite dilution, and 180 IGC tables are reported.

Additionally, tables of systems are provided here to lead the reader to further literature sources. Data are included only if numerical values were published or authors provided their numerical results by personal communication (and I wish to thank all those who did so). No digitized data have been included in this data collection. The book is the first complete overview about this subject in the world's literature. The closing day for the data collection was June, 30, 2005. The user who is in need of new additional data sets is kindly invited to ask for new information beyond this book via e-mail at [wohlfarth@chemie.uni-halle.de](mailto:wohlfarth@chemie.uni-halle.de). Additionally, the author will be grateful to users who call his attention to mistakes and make suggestions for improvements.

The *CRC Handbook of Enthalpy Data of Polymer-Solvent Systems* will be useful to researchers, specialists, and engineers working in the fields of polymer science, physical chemistry, chemical engineering, material science, biological science and technology, and those developing computerized predictive packages. The book should also be of use as a data source to Ph.D. students and faculty in Chemistry, Physics, Chemical Engineering, Biotechnology, and Materials Science Departments at universities.

Christian Wohlfarth  
Merseburg, August 2005

## About the Author

Christian Wohlfarth is Associate Professor for Physical Chemistry at Martin Luther University Halle-Wittenberg, Germany. He earned his degree in chemistry in 1974 and wrote his Ph.D. thesis on investigations on the second dielectric virial coefficient and the intermolecular pair potential in 1977, both at Carl Schorlemmer Technical University Merseburg. In 1985, he wrote his habilitation thesis, *Phase Equilibria in Systems with Polymers and Copolymers*, at Technical University Merseburg.

Since then, Dr. Wohlfarth's main research has been related to polymer systems. Currently, his research topics are molecular thermodynamics, continuous thermodynamics, phase equilibria in polymer mixtures and solutions, polymers in supercritical fluids, PVT behavior and equations of state, and sorption properties of polymers, about which he has published approximately 100 original papers. He has written the books: *Vapor-Liquid Equilibria of Binary Polymer Solutions*, *CRC Handbook of Thermodynamic Data of Copolymer Solutions*, *CRC Handbook of Thermodynamic Data of Aqueous Polymer Solutions*, and *CRC Handbook of Thermodynamic Data of Polymer Solutions at Elevated Pressures*.

He is working on the evaluation, correlation, and calculation of thermophysical properties of pure compounds and binary mixtures resulting in six volumes of the *Landolt-Börnstein New Series*. He is a respected contributor to the *CRC Handbook of Chemistry and Physics*.

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# 1. INTRODUCTION

## 1.1. Objectives of the handbook

Knowledge of thermodynamic data of polymer solutions is a necessity for industrial and laboratory processes. Furthermore, such data serve as essential tools for understanding the physical behavior of polymer solutions, for studying intermolecular interactions, and for gaining insights into the molecular nature of mixtures. They also provide the necessary basis for any developments of theoretical thermodynamic models. Scientists and engineers in academic and industrial research need such data and will benefit from a careful collection of existing data. Enthalpies of mixing and solution specially enter into energy balance and phase equilibrium calculations and are related to the structure and the energy of interaction of the molecules. They are important also from the theoretical point of view. However, the database for polymer solutions is still modest in comparison with the enormous amount of data for low-molecular mixtures, and the specialized database for enthalpies of polymer solutions is even smaller.

Basic information on polymers can be found in the *Polymer Handbook* (1999BRA), and among the solution properties, there are also short tables about systems and literature on enthalpy changes and a small table for enthalpies of solution (1999OR1, 1999OR2). The three *CRC Handbooks of Thermodynamic Data of Polymer Solutions* (2001WOH, 2004WOH, and 2005WOH) include chapters on enthalpies, i.e., for copolymer solutions, for aqueous polymer solutions, and for polymer solutions at elevated pressures. However, they provide only a minor amount of all available enthalpy data for polymer-solvent systems. No other data books or databases dedicated specially to enthalpy changes in polymer solutions presently exist. Thus, the intention of the handbook is to fill this gap and to provide scientists and engineers with an up-to-date compilation from the literature of the available enthalpy data of polymer solutions. The handbook does not present theories and models for polymer solution thermodynamics. Other publications (1990BAR, 1990FUJ, 1990KAM, 1999KLE, 1999PRA, and 2001KON) can serve as starting points for investigating those issues.

The data within this book are divided into five chapters following this introduction:

- Enthalpies of mixing or intermediary enthalpies of dilution
- Polymer partial enthalpies of mixing at infinite dilution or polymer first integral enthalpies of solution
- Solvent partial enthalpies of mixing measured by calorimetry
- Partial molar enthalpies of mixing at infinite dilution of solvents and enthalpies of solution of gases/vapors of solvents in molten polymers from inverse gas-liquid chromatography (IGC)
- Table of additional information on enthalpy effects

Data from investigations applying to more than one chapter are divided and appear in the relevant chapters. Data are included only if numerical values were published or authors provided their results by personal communication (and I wish to thank all those who did so). No digitized data have been included in this data collection. Finally, Chapter 6 covers a large number of systems in a table in which additional information on enthalpy effects in polymer solutions can be found.



## 1.2. Measurement of enthalpy changes in polymer solutions

Experiments on enthalpy changes in binary polymer solutions can be made within common microcalorimeters by applying one of the following three methods:

1. Measurement of the enthalpy change caused by solving a given amount of the solute polymer in an (increasing) amount of solvent, i.e., the solution experiment
2. Measurement of the enthalpy change caused by mixing a given amount of a concentrated polymer solution with an amount of pure solvent, i.e., the dilution experiment
3. Measurement of the enthalpy change caused by mixing a given amount of a liquid/molten polymer with an amount of pure solvent, i.e., the mixing experiment

Care must be taken for polymer solutions with respect to the resolution of the instrument, which has to be higher than for common solutions with larger enthalpic effects. Usually employed calorimeters for such purposes are the Calvet-type calorimeters based on heat-flux principle. Details can be found in 1984HEM and 1994MAR.

In particular, one has to distinguish between the following effects for polymer solutions. The enthalpy of mixing or the enthalpy of solution of a binary system is the amount of heat that must be supplied when  $n_A$  mole of pure solvent A and  $n_B$  mole of pure polymer B are combined to form a homogeneous mixture/solution in order to keep the total system at constant temperature and pressure.

$$\Delta_M H = n_A H_A + n_B H_B - (n_A H_{0A} + n_B H_{0B}) \quad (1)$$

$$\Delta_{sol} H = n_A H_A + n_B H_B - (n_A H_{0A} + n_B H_{0B}) \quad (2)$$

where:

$\Delta_M H, \Delta_{sol} H$	(extensive) enthalpy of mixing or solution
$H_A, H_B$	partial molar enthalpy of solvent A or polymer B
$H_{0A}, H_{0B}$	molar enthalpy of pure solvent A or pure polymer B
$n_A, n_B$	amount of substance of solvent A or polymer B.

From thermodynamic reasons follows that the change  $\Delta_M H$  of the molar (or specific or segment molar) enthalpy in an isothermal-isobaric mixing process is also the molar (or specific or segment molar) excess enthalpy,  $H^E$ , of the mixture. The dependence of  $H^E$  upon temperature,  $T$ , and pressure,  $P$ , permits the correlation of such data with excess heat capacities,  $C_p^E$ , and excess volumes,  $V^E$ .

$$\left( \partial H^E / \partial T \right)_P = C_p^E \quad (3)$$

$$\left( \partial H^E / \partial P \right)_T = V^E - T \left( \partial V^E / \partial T \right)_P \quad (4)$$

where:

$C_p^E$	excess heat capacity
$H^E$	excess enthalpy = $\Delta_M H$ = enthalpy of mixing
$P$	pressure
$T$	(measuring) temperature
$V^E$	excess volume at temperature $T$ .

The enthalpy effect might be positive (endothermic solution/mixture) or negative (exothermic solution/mixture) depending on the ratio  $n_A/n_B$ , i.e., the concentration of the total system. Unfortunately, in some of the older literature, the definition of the sign of the so-called (*integral*) *heat of solution* is reversed, compared with the enthalpy, occasionally causing some confusion. The value of the enthalpy of solution is dependent on the degree of crystallinity for semicrystalline polymers and, usually to a lesser extent, on the thermal history of glassy polymers. The enthalpy of mixing is independent of any crystalline or glassy aspects of the polymer. Thus, the enthalpy of mixing can be obtained without difficulties only for liquid/molten polymers mixed with a solvent.

The melting enthalpy of the crystallites and/or the glass enthalpy have to be determined additionally by independent measurements. As such a procedure is rather difficult and might cause substantial errors, it is common to measure the intermediary enthalpy of dilution, i.e., the enthalpy effect obtained if solvent A is added to an existing homogeneous polymer solution. The extensive intermediary enthalpy of dilution is the difference between two values of the enthalpy of the polymer solution corresponding to the concentrations of the polymer solution at the beginning and at the end of the dilution process:

$$\Delta_{dil}H^{12} = H^{(2)} - H^{(1)} \quad (5)$$

with

$$H^{(1)} = n_A^{(1)}H_A^{(1)} + n_BH_B^{(1)} \quad (6)$$

$$H^{(2)} = n_A^{(2)}H_A^{(2)} + n_BH_B^{(2)} \quad (7)$$

and

$$n_A^{(2)} = n_A^{(1)} + \Delta n_A \quad (8)$$

where:

$\Delta_{dil}H^{12}$	(extensive) intermediary enthalpy of dilution
$H^{(1)}, H^{(2)}$	enthalpies of the polymer solution before and after the dilution step
$H_A^{(1)}, H_A^{(2)}$	partial molar enthalpies of solvent A before and after the dilution step
$H_B^{(1)}, H_B^{(2)}$	partial molar enthalpies of polymer B before and after the dilution step
$n_A^{(1)}$	amount of solvent in the solution before the dilution step
$n_A^{(2)}$	amount of solvent in the solution after the dilution step
$\Delta n_A$	amount of solvent added to solution (1)
$n_B$	amount of polymer in all solutions.

$\Delta_{dil}H^{12}$  is not directly related to  $\Delta_M H$  but to  $(\partial \Delta_M H / \partial n_A)_{P,T,n_j}$  by:

$$\Delta_{dil}H^{12} = \int_{n_A^{(1)}}^{n_A^{(2)}} (\partial \Delta_M H / \partial n_A)_{P,T,n_j} dn_A \quad (9)$$

The term *integral* is often added to these enthalpy changes to describe changes where finite amounts of substances are mixed. Especially, the *integral enthalpy of solution/mixing for a polymer B* is given in a number of literature sources by applying the following two definitions:

• *per mole* polymer B:

$$^{int} \Delta_{sol} H_B = \Delta_{sol} H / n_B \quad (10)$$

$$^{int} \Delta_M H_B = \Delta_M H / n_B \quad (11)$$

• per gram polymer B (where the intensive  $\Delta H$ s are the specific ones):

$${}^{int}\Delta_{sol}H_B = \Delta_{sol}H/m_B \quad (12)$$

$${}^{int}\Delta_M H_B = \Delta_M H/m_B \quad (13)$$

where:

${}^{int}\Delta_{sol}H_B$	integral enthalpy of solution of polymer B
${}^{int}\Delta_M H_B$	integral enthalpy of mixing of polymer B
$m_B$	mass of polymer B
$n_B$	amount of substance of polymer B.

As stated above, the difference between  ${}^{int}\Delta_{sol}H_B$  and  ${}^{int}\Delta_M H_B$  is determined by any enthalpic effects caused from solid-liquid phase transition of the crystallites and/or from glass transition and is zero for liquid/molten polymers.

The term *differential* is sometimes added to enthalpy changes where infinitesimal (i.e., very small) amounts were added to a very large amount of either solution or pure component. These enthalpy changes are usually called *partial* (molar or specific) enthalpies of solution/mixing:

$$\Delta_{sol}H_B = (\partial\Delta_{sol}H / \partial n_B)_{P,T,n_j} = H_B - H_{0B} \quad (14)$$

$$\Delta_M H_B = (\partial\Delta_M H / \partial n_B)_{P,T,n_j} = H_B - H_{0B} \quad (15)$$

with a unit of J/mol. However, for polymer solutions,  $\Delta_{sol}H_B$  or  $\Delta_M H_B$  is often expressed as the enthalpy change per unit mass of polymer added which can be obtained from the following derivative:

$$\Delta_{sol}H_B = (\partial\Delta_{sol}H / \partial m_B)_{P,T,m_j} \quad (16)$$

$$\Delta_M H_B = (\partial\Delta_M H / \partial m_B)_{P,T,m_j} \quad (17)$$

where:

$\Delta_{sol}H_B$	partial molar (or specific) enthalpy of solution of polymer B
$\Delta_M H_B$	partial molar (or specific) enthalpy of mixing of polymer B

with a unit of J/g. Similar to these definitions one can find results related to one mole of monomers (or base units). The derivative is then made by applying the base mole fraction of the polymer. The partial (molar or specific) enthalpy of solution of the polymer B is equal to the so-called differential enthalpy of solution at finite concentrations which is, for finite concentrations, different from the  ${}^{int}\Delta_{sol}H_B$  or  ${}^{int}\Delta_M H_B$  data as defined above. For example, in the case of a binary mixture, one obtains the relation:

$$\Delta_M H_B = \Delta_M H + (1 - x_B)(\partial\Delta_M H / \partial x_B) \quad (18)$$

which results in different values to  ${}^{int}\Delta_M H_B$ .

In the case of adding an infinitesimal amount of polymer to the pure solvent, the partial (molar or specific) enthalpy of solution of the polymer B is properly identified as the partial enthalpy of solution of the polymer at infinite dilution,  $\Delta_{sol}H_B^\infty$ , or the partial enthalpy of mixing of the polymer at infinite dilution,  $\Delta_M H_B^\infty$ . Its value at infinite dilution of the polymer is equal to the so-called *first* integral enthalpy of solution (unfortunately, sometimes referred to more simply as the enthalpy of solution of the polymer, but, as discussed above, identical values can only be obtained for infinite dilution). In practice, the partial (molar or specific) enthalpy of solution of the polymer B is measured by mixing isothermally a large excess of pure solvent and a certain amount of the polymer to form a homogeneous solution.

The state of the polymer before dissolution can significantly affect the enthalpy of solution. An amorphous polymer below its glass transition temperature  $T_g$  often dissolves with the release of heat. The enthalpy of solution of a glassy polymer is usually dependent on temperature and, to some extent, on the thermal history of the glass-forming process. An amorphous polymer above  $T_g$  can show endothermic or exothermic dissolution behavior depending on the nature of the solvent and the interaction energies involved as is the case for any enthalpy of mixing. The dissolving of a semicrystalline polymer requires an additional amount of heat associated with the disordering of crystalline regions. Consequently, its enthalpy of solution is usually positive and depends on the degree of crystallinity of the polymer sample.

The mathematical definition for the partial molar enthalpies of solution/mixing is given for the solvent A by:

$$\Delta_{sol}H_A = (\partial \Delta_{sol}H / \partial n_A)_{P,T,n_j} = H_A - H_{0A} \quad (19)$$

$$\Delta_M H_A = (\partial \Delta_M H / \partial n_A)_{P,T,n_j} = H_A - H_{0A} \quad (20)$$

where:

$\Delta_{sol}H_A$	partial molar enthalpy of solution of solvent A
$\Delta_M H_A$	partial molar enthalpy of mixing of solvent A (= differential enthalpy of dilution)
$n_A$	amount of substance of solvent A

again with a unit of J/mol. The partial molar enthalpy of solution/mixing is equal to the so-called differential enthalpy of dilution as a consequence of adding an infinitesimal amount of solvent to the solution/mixture. The *integral enthalpy of dilution for the solvent A* is equivalent to the integral molar enthalpy of mixing for the solvent A as defined by:

$$^{int} \Delta_M H_A = \Delta_M h / n_A \quad (21)$$

and, in the case of adding a very small amount of solvent to the pure polymer, the partial molar enthalpy of solution at infinite dilution of the solvent is obtained. Partial molar enthalpies of mixing (or dilution) of the solvent are included in this data collection only for cases where they were obtained from calorimetric experiments.

Generally, it is known that partial molar enthalpies of mixing (or dilution) of the solvent can also be determined from the temperature dependence of the activity of the solvent,  $a_A$ :

$$\Delta_M H_A = R [\partial \ln a_A / \partial (1/T)]_P \quad (22)$$

where:

$a_A$	activity of solvent A
$P$	pressure
$T$	(measuring) temperature.

Enthalpy data from light scattering, osmometry, vapor pressure or vapor sorption measurements, and demixing experiments can be found in the literature. However, agreement between enthalpy changes measured by calorimetry and results determined from the temperature dependence of solvent activity data is often of limited quality. Therefore, such data are not included here, but, Chapter 6 provides a number of systems in which such additional information on enthalpy effects in polymer solutions can be found.

From engineering and also from scientific aspects, the partial molar enthalpy of mixing at infinite dilution of the solvent in the liquid/molten polymer  $\Delta_M H_A^\infty$  is of value. Therefore, data for  $\Delta_M H_A^\infty$  determined by *inverse gas-liquid chromatography* (IGC) have been included here.

$$\Delta_M H_A^\infty = R [\partial \ln \Omega_A^\infty / \partial (1/T)]_p \quad (23)$$

where:

$\Delta_M H_A^\infty$  partial molar enthalpy of mixing at infinite dilution of solvent A  
 $\Omega_A^\infty$  mass fraction-based activity coefficient of solvent A in the liquid phase with  
 $a_A = w_A \Omega_A$  at infinite dilution.

Additionally, the enthalpies of solution at infinite dilution  $\Delta_{sol} H_{A(vap)}^\infty$  of solvent vapor in molten polymers determined by IGC have been included.

$$\Delta_{sol} H_{A(vap)}^\infty = -R [\partial \ln V_g^0 / \partial (1/T)]_p \quad (24)$$

where:

$\Delta_{sol} H_{A(vap)}^\infty$  first integral enthalpy of solution of the vapor of solvent A  
 (with  $\Delta_{sol} H_{A(vap)}^\infty = \Delta_M H_A^\infty - \Delta_{LV} H_{0A}$ )  
 $V_g^0$  specific retention volume corrected to 0°C.

The equipment for IGC does not differ in principle very much from that used in analytical GLC. For operating at infinite dilution, the carrier gas flows directly to the column that is inserted into a thermostatted oil bath (to get a more precise temperature control than in a conventional GLC oven). The output of the column is measured with a flame ionization detector or alternately with a thermal conductivity detector. Helium is used today as the carrier gas (nitrogen was used in earlier work). From the difference between the retention time of the injected solvent sample and the retention time of a non-interacting gas (marker gas), thermodynamic equilibrium data can be obtained. Most experiments were done up to now with packed columns, but capillary columns were used too. The experimental conditions must be chosen so that real thermodynamic data can be obtained, i.e., equilibrium bulk absorption conditions. Errors caused by unsuitable gas flow rates, unsuitable polymer loading percentages on the solid support material and support surface effects as well as any interactions between the injected sample and the solid support in packed columns, unsuitable sample size of the injected probes, carrier gas effects, and imprecise knowledge of the real amount of polymer in the column, can be sources of problems, whether data are nominally measured under real thermodynamic equilibrium conditions or not, and have to be eliminated. The sizeable pressure drop through the column must be measured and accounted for. An additional condition for obtaining real thermodynamic equilibrium data is caused by the nature of the polymer sample. Thermodynamic equilibrium data require the polymer to be in a molten state. This means that IGC measurements have to be performed for this purpose well above the glass transition temperature of the amorphous polymer or even above the melting temperature of the crystalline parts of a polymer sample. As a rule, the experimental temperature must exceed the glass transition or the melting temperature by about 50 K.

The *data reduction for infinite dilution IGC* starts with the usually obtained parameters of retention volume or net retention volume which have to be calculated from the measured retention times and the flow rate of the carrier gas at column conditions.

$$V_{net} = V_r - V_{dead} \quad (25)$$

where:

$V_{net}$	net retention volume
$V_r$	retention volume
$V_{dead}$	retention volume of the inert marker gas, dead retention, gas holdup.

These net retention volumes are reduced to specific retention volumes,  $V_g^0$ , by division of equation (1) with the mass of the liquid (here the liquid is the molten polymer). They are corrected for the pressure difference between column inlet and outlet pressure, and reduced to a temperature  $T_0 = 273.15$  K.

$$V_g^0 = \left( \frac{V_{net}}{m_B} \right) \left( \frac{T_0}{T} \right) \frac{3(P_{in}/P_{out})^2 - 1}{2(P_{in}/P_{out})^3 - 1} \quad (26)$$

where:

$V_g^0$	specific retention volume corrected to $0^\circ\text{C} = 273.15$ K
$m_B$	mass of the polymer in the liquid phase within the column
$P_{in}$	column inlet pressure
$P_{out}$	column outlet pressure
$T$	measuring temperature
$T_0$	reference temperature = 273.15 K.

The activity coefficient at infinite dilution reads, if we neglect interactions to and between carrier gas molecules (which are normally helium):

$$\Omega_A^\infty = \left( \frac{RT_0}{V_g^0 M_A P_A^s} \right) \exp \left[ \frac{(B_{AA} - V_A^L)(P - P_A^s)}{RT} \right] \quad (27)$$

where:

$B_{AA}$	second virial coefficient of pure solvent A at temperature $T$
$M_A$	molar mass of solvent A
$P_A^s$	saturation vapor pressure of pure liquid solvent A at temperature $T$
$R$	gas constant
$T_0$	reference temperature = 273.15 K
$V_A^L$	molar volume of pure liquid solvent A at temperature $T$ .

More detailed information on the application of IGC to polymer solutions and the corresponding estimation of enthalpic data can be found in a number of books (e.g., 1976NES, 1988NES, 1989LLO, 1989VIL, 1991MUN).



### 1.3. Guide to the data tables

#### Characterization of the polymers

Polymers vary by a number of characterization variables. The molar mass and their distribution function are the most important variables. However, tacticity, sequence distribution, branching, and end groups determine their thermodynamic behavior in solution too. Unfortunately, much less information is provided with respect to the polymers that were applied in most of the thermodynamic investigations in the original literature. For copolymers, the chemical distribution and the average chemical composition are also to be given. In many cases, the samples are characterized only by one or two molar mass averages and some additional information (e.g.,  $T_g$ ,  $\rho$ , or how and where it was synthesized). Sometimes even this information is missing.

The molar mass averages are defined as follows:

number average  $M_n$

$$M_n = \frac{\sum_i n_{B_i} M_{B_i}}{\sum_i n_{B_i}} = \frac{\sum_i w_{B_i}}{\sum_i w_{B_i} / M_{B_i}} \quad (28)$$

mass average  $M_w$

$$M_w = \frac{\sum_i n_{B_i} M_{B_i}^2}{\sum_i n_{B_i} M_{B_i}} = \frac{\sum_i w_{B_i} M_{B_i}}{\sum_i w_{B_i}} \quad (29)$$

z-average  $M_z$

$$M_z = \frac{\sum_i n_{B_i} M_{B_i}^3}{\sum_i n_{B_i} M_{B_i}^2} = \frac{\sum_i w_{B_i} M_{B_i}^2}{\sum_i w_{B_i} M_{B_i}} \quad (30)$$

viscosity average  $M_\eta$

$$M_\eta = \left( \frac{\sum_i w_{B_i} M_{B_i}^a}{\sum_i w_{B_i}} \right)^{1/a} \quad (31)$$

where:

$a$	exponent in the viscosity-molar mass relationship
$M_{B_i}$	molar mass of polymer species $B_i$
$n_{B_i}$	amount of substance of polymer species $B_i$
$w_{B_i}$	mass fraction of polymer species $B_i$ .

### Measures for the polymer concentration

The following concentration measures are used in the tables of this handbook (where B always denotes the polymer, A denotes the solvent, and in ternary systems C denotes the third component):

*mass/volume concentration:*

$$c_A = m_A/V \quad c_B = m_B/V \quad (32)$$

*mass fraction:*

$$w_A = m_A/\sum m_i \quad w_B = m_B/\sum m_i \quad (33)$$

*mole fraction:*

$$x_A = n_A/\sum n_i \quad x_B = n_B/\sum n_i \quad \text{with } n_i = m_i/M_i \text{ and } M_B = M_n \quad (34)$$

*volume fraction:*

$$\varphi_A = (m_A/\rho_A)/\sum (m_i/\rho_i) \quad \varphi_B = (m_B/\rho_B)/\sum (m_i/\rho_i) \quad (35)$$

*segment fraction:*

$$\psi_A = x_A r_A / \sum x_i r_i \quad \psi_B = x_B r_B / \sum x_i r_i \quad \text{usually with } r_A = 1 \quad (36)$$

*base mole fraction:*

$$z_A = x_A r_A / \sum x_i r_i \quad z_B = x_B r_B / \sum x_i r_i \quad \text{with } r_B = M_B/M_0 \text{ and } r_A = 1 \quad (37)$$

where:

$c_A$	(mass/volume) concentration of solvent A
$c_B$	(mass/volume) concentration of polymer B
$m_A$	mass of solvent A
$m_B$	mass of polymer B
$M_A$	molar mass of solvent A
$M_B$	molar mass of polymer B
$M_{Bi}$	molar mass of polymer species $B_i$
$M_n$	number-average relative molar mass
$M_0$	molar mass of a basic unit of polymer B
$n_A$	amount of substance of solvent A
$n_B$	amount of substance of polymer B
$n_{Bi}$	amount of substance of polymer species $B_i$ with molar mass $M_{Bi}$
$r_A$	segment number of solvent A, usually $r_A = 1$
$r_B$	segment number of polymer B
$V$	volume of the liquid solution at temperature $T$
$w_A$	mass fraction of solvent A
$w_B$	mass fraction of polymer B
$w_{Bi}$	mass fraction of polymer species $B_i$ with molar mass $M_{Bi}$

$x_A$	mole fraction of solvent A
$x_B$	mole fraction of polymer B
$z_A$	base mole fraction of solvent A
$z_B$	base mole fraction of polymer B
$\varphi_A$	volume fraction of solvent A
$\varphi_B$	volume fraction of polymer B
$\rho_A$	density of solvent A
$\rho_B$	density of polymer B
$\psi_A$	segment fraction of solvent A
$\psi_B$	segment fraction of polymer B.

For high-molecular polymers, a mole fraction is not an appropriate unit to characterize composition. However, for oligomeric products with rather low molar masses, mole fractions were sometimes used. In the common case of a distribution function for the molar mass,  $M_B = M_n$  is to be chosen. Mass fraction and volume fraction can be considered as special cases of segment fractions depending on the way by which the segment size is actually determined:  $r_i/r_A = M_i/M_A$  or  $r_i/r_A = V_i/V_A = (M_i/\rho_i)/(M_A/\rho_A)$ , respectively. Classical segment fractions are calculated by applying  $r_i/r_A = V_i^{\text{vdW}}/V_A^{\text{vdW}}$  ratios where hard-core van der Waals volumes,  $V_i^{\text{vdW}}$ , are taken into account. Their special values depend on the chosen equation of state (or simply some group contribution schemes, e.g., 1968BON, 1990KRE) and have to be specified.

Volume fractions imply a temperature dependence and, as they are defined in equation (35), neglect excess volumes of mixing and, very often, the densities of the polymer in the state of the solution are not known correctly. However, volume fractions can be calculated without the exact knowledge of the polymer molar mass (or its averages).

Base mole fractions are sometimes applied for polymer systems in earlier literature. The value for  $M_0$  is the molar mass of a basic unit of the polymer. Sometimes it is chosen arbitrarily, however, and has to be specified.

### Experimental data tables

The data tables in each chapter are provided in order of the names of the polymers. In this data book, mostly source-based polymer names are applied. These names are more common in use, and they are usually given in the original sources, too. Structure-based names, details about their nomenclature can be found in the *Polymer Handbook* (1999BRA), are chosen in some single cases only. CAS index names for polymers are not applied here. Finally, a list of the polymers in the appendix utilizes the names as given in the chapters of this book.

Within types of polymers, the individual samples are ordered by their increasing average molar mass, and, when necessary, systems are ordered by increasing temperature. Within data sets for equal polymers, systems are ordered by the names of the solvents. In ternary systems, ordering is additionally made subsequently according to the name of the third component in the system.