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SOLUBILITY OF POLYMERS

Introduction

The process of dissolving a pure polymer begins with solvent molecules permeating bulk polymer. Usually, this requires more energy and is slower if the polymer is crystalline than if it is liquid, rubbery or glassy. The polymer near the interface swells to accommodate the incoming molecules of solvent while individual long-chain molecules may be freed from near the interface and diffuse into the solvent phase. If the solubility limit is not exceeded, the system eventually becomes homogeneous. The extent to which the solution process can occur depends especially on the temperature, the chemical nature of solute and solvent, the molecular weight of the polymer, and on the degree of crystallinity for semi crystalline polymers.

There is an exception to this description. If the polymer is a cross-linked network, the polymer can imbibe solvent and swell, but only to a limited extent. Because all structural units in the polymer are interconnected by chemical bonds, there is a point beyond which the units cannot be further dispersed with the continued addition of solvent. If this limit is exceeded, the equilibrium state is a two-phase system comprising a saturated polymer gel and the excess pure solvent.

Generally, polymers are less likely to be soluble in a specified liquid than are their low molecular weight analogues; the solubility of most polymers decreases as their molecular weight rises. Phase diagrams depicting demixing temperatures as a function of the weight fraction of amorphous polymers are skewed; the region of limited miscibility typically occurs at low concentrations of polymer rather than near the middle of the phase diagram. Consequently, mixing polymer with a poor solvent sometimes leads to a highly swollen polymer phase in equilibrium with almost pure solvent. As with mixtures of low molecular weight liquids, the solubility of polymers often increases with rising temperature.

The saying "Like dissolves like" ("*Similia similibus solvuntur*") applies to polymer solutions as well as to liquid mixtures of small molecules. For example, polar liquids are more likely to be better solvents for polar polymers than are nonpolar liquids, and aromatic liquids are more likely to dissolve a polymer that is predominantly aromatic than are aliphatic liquids. Also, solution is favored when specific interactions such as hydrogen bonding are formed between solvent and polymer.

The solubility of polymers is important for both practical and theoretical reasons. Solubility is one of the considerations in setting the conditions for

polymerization. Solutions of polymer are used extensively in processing, eg, the spinning of fibers and the drawing of films. The utility of additives such as plasticizers, antioxidants, and colorants may depend on their solubility in bulk polymer. Polymer solubility is also an important consideration in the coatings and adhesives industries. Most methods of polymer analysis are based on measurements of their solution, such as light scattering, osmometry, gel-permeation chromatography, and viscometry. On the other hand, there are some applications in which polymer solubility may be undesirable, in which case it is important to understand solubility in order to determine how to minimize mixing. For example, swelling and crazing due to the presence of solvents can lead to unwanted changes in bulk polymer.

The almost unlimited possibilities of polymers for discrimination, as compared with low molecular weight compounds, bear important consequences for their solubility. It is the extremely high variability in their molecular structure that makes this class of substances so unique. In order to characterize a given polymer, one needs to specify at least the following items: chemical nature of the monomer units and in some cases also of the end groups, molecular weight, molecular weight distribution plus details of the molecular architecture (linear, branched, etc). In the case of copolymers, the situation becomes even more complicated in view of the different possibilities to incorporate further types of monomeric units into the polymer chains.

Because of the large number of additional variables it is impossible to cover the solution behavior of each individual representative of a certain group of polymers. For homopolymers the most general information that can be supplied concerns the temperature/pressure regions, within which they mix homogeneously with the solvent, irrespective of the molecular weight of the polymer and of the mixing ratio of the components. However, in most instances the published data refer to special cases only. This means that the data presented in the tables need to be applied with a certain minimum of thermodynamic expertise. In view of the vast literature existing in the field, polymers of complex structure (like dendrimers or copolymers) and some phenomena (like three phase equilibria) are excluded.

This article is structured in the following way: An introductory section recalls the essentials of phenomenological thermodynamics to the extent they are required for the solubility of polymers. In all cases numbers are used to denote low molecular weight substances and letters for polymers in order to promote rapid comprehension. The next parts describe the different experimental methods, which are required for solubility studies and shows some representative phase diagrams. The subsequent section deals with the modeling of solubilities and compares experiment and theory. Tables with solubility data are presented in the final chapter.

Phenomenological Thermodynamics

The theoretical study of phase equilibria started more than a century ago with the pioneering work of Gibbs (1,2) and was subsequently fostered for a large variety of cases by Bakhuis Roozeboom (3,4). The present state concerning phase

diagrams for polymer containing mixtures is being described in a contemporary textbook (5). The pivotal property of all these considerations is the Gibbs energy, G, of a system, which provides an adequate criterion to decide (for isobaric and isothermal conditions) whether two or more components form a homogenous, molecularly disperse mixture in the equilibrium state, or whether two or more phases coexist under these conditions. According to the Gibbs-Helmholtz equation G is made up by an enthalpy (H) and by an entropy (S) contribution as follows

$$G = H - TS \tag{1}$$

where T represents the absolute temperature. Under equilibrium conditions G assumes its minimum value.

For the mixing or demixing processes under consideration this criterion enables the formulation of some general (i.e. model independent) conditions for the establishment of liquid/liquid and of liquid/solid phase equilibria. In case of polymer containing systems the *molar* quantities, normally used for low molecular weight mixtures, become inadequate (1 mol of a typical polymer amounts to 1 ton) and they are therefore replaced by *segment molar* quantities. Within reasonable limits the size of a segment can be defined freely. For polymer *solutions* it is usually the volume of the solvent which is chosen for that purpose; for polymer *blends* a value of 100 mL/segment is customary. Once the size of a segment is fixed, the number of segments N_i, a certain component i is made of, can be calculated by means of the volume of component i according to

$$N_i = \frac{\bar{V}_i}{\bar{V}_{seg}} \tag{2}$$

In this relation the bars above the symbols signify molar quantities. The segment fractions σ_i of component i in a mixture consisting of j components are then calculated as

$$\sigma_i = \frac{n_i N_i}{\sum_j n_j N_j} \approx \varphi_i \tag{3}$$

where n designates the number of moles. As long as the excess volumes of mixing remain small, it is possible to use volume fractions φ instead of segment fractions (the volume of the segment cancels). Segment molar quantities (indicated by double bar superscripts) are obtained dividing the respective extensive quantity by the total number of segments in the mixture. For the segment molar Gibbs energy and a binary mixture this means

$$\bar{\bar{G}} = \frac{G}{n_1 N_1 + n_2 N_2} \tag{4}$$

The segment molar Gibbs energy of a *molecularly disperse mixture* (normalized to the thermal energy RT) may depend on composition in three clearly distinguishable ways as shown for polymer solutions in Fig. 1. This graph is drawn under the assumption that the pure components are liquid under the given conditions; if this is not the case one needs to account for the corresponding changes

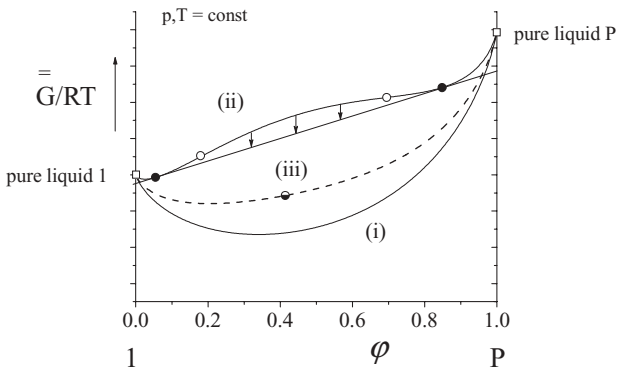

Fig. 1. Three qualitatively distinguishable composition dependencies of the reduced segment molar Gibbs energy for mixtures of a liquid polymer P and liquid solvent 1. (i): Complete miscibility of the components. (ii): Coexistence of two liquids (with the compositions indicated by the full circles) and two points of inflection (open circles). (iii): Occurrence of a critical point (half filled circle).

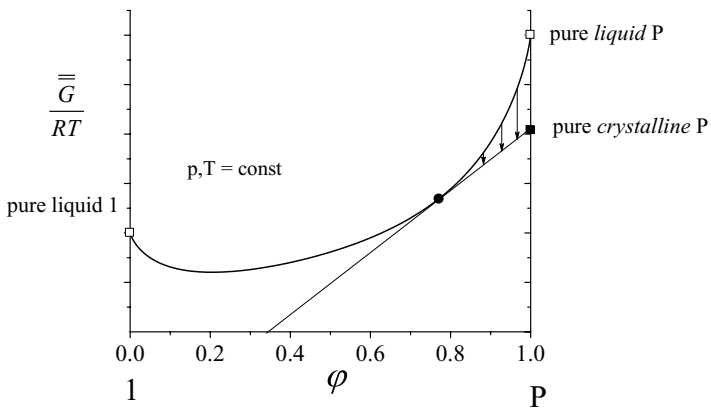

Fig. 2. Composition dependence of the reduced segment molar Gibbs energy for mixtures of a solid, crystalline polymer and a liquid solvent.

in G caused by melting, as discussed in the context of Fig. 2 for a crystalline polymer. The three options depicted in Table 1 are the following: (i) The curve is – irrespective of the composition of the mixture – always located above the tangent or (ii) within a certain φ range it runs below it and exhibits two points of inflection, where these φ values are denoted spinodal compositions, and, finally (iii), in a very special case the curve exhibits a flat point, i.e. the second *and* the third derivatives becomes zero at a characteristic composition, the so called critical point.

If the Gibbs energy varies with composition as depicted in curve (i) of Fig. 1, polymer and solvent are miscible in all ratios, because at no concentration there exists a possibility to lower the Gibbs energy. With case (ii), on the other hand, there is a composition range (located between the full circles) within which such a reduction can be realized as indicated by the arrows. Two phases are formed

Table 1. Solvents/non-solvents

Polymer	Solvent	Non-solvent	References
polystyrene	$SbCl_3$, $AsCl_3$, cyclohexane (above 35°C), benzene, ethylbenzene, CH_2Cl_2,$CHCl_3$, chlorobenzene, cyclohexanone, methyl ethyl ketone, dimethyl formamide, ethyl acetate, methyl benzoate, 1,3-dioxolane, methyl to butyl phthalate, 1-nitropropane, pyridine CS_2	heptane, acetone, methanol, propanol, diethyl ether, glycol ether, methyl acetate(swelling), organic acids, phenol, tricresyl phosphate, tetra-/ penta-/ hexafluorobenzene	(58)
poly(methyl methacrylate)	acetone, ethyl actetate, ethylene-chloride, ethyl glycol, amyl acetate, chlorobenzene, cyclohexanone, benzene, butyl acetate, dioxane, methyl acetate, butan-2-one, methylene chloride, methyl glycol, nitroethane, toluene, trichloroethylene, acetic acid	aliphatic and cycloaliphatic hydrocarbons (heptane, decahydronaphthalene), ethanol (water free), ethylene- and butylene glycol, diethyl ether (swelling), butanol, butyl glycol, methanol, CS_2, CCl_4, xylene (swelling) formamide, octanol	(59,60)
poly(vinyl chloride)	$SbCl_3$, cyclohexanone, cyclopentanone, diisopropylketone, butan-2-one, isophorone, dichlorobenzene, trichlorobenzene, dimethylformamide, mesityl oxide, nitrobenzene, tetrahydrofuran, hexamethyl phosphoric acid triamide, tricresyl phosphate, mixtures of acetone	aliphatic, cycloaliphatic and aromatic hydrocarbons, methanol, ethanol, butanol, diethyl ether, acetic acid, acetic acid anhydride, methyl- and ethyl acetate, glycols, CS_2, vinyl chloride, acetone (swelling), nitromethane (swelling), hydrazine, PCl_3, POCl	(58,61,62)
poly(ethylene carbonate)	$CHCl_3$, acetone, cyclohexanone, dimethyl formamide, tetrahydrofuran, 1,4-dioxane, dimethyl sulfoxide	aliphatic and aromatic hydrocarbons, *o*-dichloro benzene, diethyl ether, methanol	(63)
poly(ethylene glycol)	acetonitrile, ethylene carbonate, ethylene dichloride, benzene, chloroform, dimethylformamide, methanol, butanone, dichloromethane, carbon tetrachloride, tetrahydrofuran, trichloroethylene, water (cold); at slightly elevated temperatures also in acetone,	aliphatic hydrocarbons, ethylene glycol, 1,3-butandiol, diethyl ether, diethylene glycol, water (hot)	(64)

poly(propylene glycol)	polyethylene glycol, aqueous solutions of urea, benzene, toluene	similar to poly(ethylene glycol), 2-amino ethanol, ethyl acetate (swelling), diethyl ether (swelling), dimethylformamide, methanol	(58,64–66)
poly(*N*-vinylpyrrolidone)	water, in the presence of small amounts of water (less than 5%): CH_2Cl_2, $CHCl_3$, methanol, ethanol, butanol, ethylene glycol, glycerol, ethanolamine, butylamine, aniline, pyridine, morpholine, dimethylformamide, 2-pyrrolidone, N-methyl-2-pyrrolidone	aliphatic, cycloaliphatic and aromatic hydrocarbons, carbontetrachloride, CH_3CCl_3, CH_2Cl_3, chlorotoluene, ethyl- butyl- and amyl acetate, diethyl ether, 1,4-dioxane, acetone (swelling), PCl_3, $POCl_3$, $SOCl_2$	(58,67–69)
poly(vinyl methyl ether) (atactic)	methanol, ethanol, benzene, 1,4-dioxane,methyl acetate, ethyl acetate, butyl actetate, chloroform, carbon tetrachloride, chlorobenzene, acetone, butan-2-one, cyclohexanone, tetrahydrofruran, water (cold)	ethylene glycol, hexane, diethylether, water (hot)	(70)
poly(vinyl methyl ether) (isotactic)		heptane, methanol, water	(71,72)
polymethylacrylate	benzene, toluene, CH_2Cl_2, $CHCl_3$, $C_2H_4Cl_2$, $C_2H_3Cl_3$, chlorobenzene, methyl acetate, ethyl acetate, butyl acetate, amyl acetate, acetone, butan-2-one, cyclohexanone, tetrahydrofuran, 1,4-dioxane, mixtures of ethanol/water, PCl_3, $POCl_3$, $SOCl_2$, liquid SO_2	aliphatic and cycloaliphatic hydrocarbons, carbon tetrachloride, tetrahydronaphthalene, diethylether, methanol, ethanol, butyl glycol, CS_2, xylene (swelling)	(58)
polyacrylonitril	hexanedinitrile, ethylene carbonate, $SbCl_3$, gamma-butyrolactone, epsilon-caprolactam, cyanoacetic acid, dimethyl actetamide, dimethylformamide, dimethyl sulfone, dimethyl sulfoxide, hexafluoroacetone sesquihydrate, hydroxyacetonitrile, propanedinitrile	acetonitrile, acrylonitrile, aliphatic, cycloaliphatic and aromatic hydrocarbons, halogenated aliphatic and aromatic hydrocarbons, alcohols, $AsCl_3$, diethylether, methyl acetate, ethyl acetate, formamide, acetone, mixtures of propanedinitrile/dimethyl form	(73,74)

(Continued)

Table 1. ***(Continued)***

Polymer	Solvent	Non-solvent	References
poly(vinyl alcohol) (atactic)	diethylenetriamine (cold), triethylenediamine, triethylenetetramine (cold), dimethyl sulfoxide (hot) glycols (hot), glycerol, hexafluoroacetone sesquihydrate, water, formamide, dimethylformamide	aliphatic, cycloaliphatic, and aromatic hydrocarbons, methanol, ethanol and higher alcohols, diethylether, 1,4-dioxane, acetic acid, methyl acetate and higher esters, halogenated aliphatic and aromatic hydrocarbons, aceton and higher ketones, tetrahydrofuran	(70)
poly ethylene, high density (HDPE)	soluble only above 80°C in aliphatic, aromtic, and cycloaliphatic hydrocarbons (eg, decane *p*-xylene, decahydronaphthalene), halogenated aliphatic, aromatic, and cycloaliphatic hydrocarbons (eg, heptylchloride, dichlorobenzene, chlorocyclohexane)	insoluble in all substanzes at room temperature, at higher temperatures also insoluble in polar compounds with acyl groups smaller than butyl (propanol, butan-2-one, propyl acetate), inorganic comounds	(70)
polyethylene low density (LDPE)	like HDPE, the temperature of solubility lies normally 20–30°C lower depending on the degree of branching	like HDPE	(70)
polytetrafluorethylene	perfluoroketoses at 350°C; SF_5NCS for small molecular weights	all other substances	(70)
cellulose	concentrated aqueous solutions of HF, HCl, HBr, H_2SO_4, H_3PO_4, $ZnCl_2$, $Ca(SCN)_2$ (always with degradation); aqueous solution of tetraethylammonium hydroxide, benzyltrimethylammonium hydroxide, dimethyldibenzylammonium hydroxide, tetraalkyphosphonium hydroxide	organic solvents, water (swelling)	(70)
hydroxyethyl starch (DS 0.3–0.4)	water (cold)		(70)

polydimethylsiloxane (highly viscous)	aliphatic, cycloaliphatic, and aromatic hydrocarbons, CH_2Cl_2, $CHCl_3$, CCl_4, C_2Cl_4, C_2HCl_3, n-C_4H_9Cl, C_2H_5Br, chlorobenzene, p-chlorotoluene, o-dichlorobenzene, o-fluorotoluene, diethyl ether, 1,2-dimethoxyethane, phenetole, methyl ethyl ketone, diethylketone	in acetone, ethanol, isopropanol, butanol, and dioxane partial soluble; unsoluble in dimethylnaphthalene, $C_2H_4Cl_2$, $C_4H_8Br_2$, 1-bromododecane, bromobenzene, p-bromotoluene, diphenyl ether, mesityl oxide, acetophenone, methylacetophenone, g-butyrolactone	(70)
polyhexamethylene adipinamide (Nylon-6:6)	HCOOH, chloroacetic acid, HF, H_3PO_4, H_2SO_4, phenols, trichloroethanol, trifluoroethanol, chloral hydrate, SO_2, methanolic HCl-, $CaCl_2$-, and $MgCl_2$-solutions; furthermore between 120, and 180°C: ethylene chlorohydrin, N-acetylmorpholine, benzyl alcohol	similar to poly-e-caprolactam; diisobutylketon, methylacetophenone, biphenyl, diphenyl ether, water	(75)
poly-e-caprolactam (nylon-6)	formic acid, $SbCl_3$, $AsCl_3$, ethylene carbonate, benzyl alcohol, g-butyrolactone, chlorinated acetic acid, chlorophenol, dimethyl formamide, dimethyl sulfoxide, formamide, hexafluoroacetone sesquihydrate, phenethyl alcohol, phosphoric acid trisdimethyl amide	aliphatic, cycloaliphatic, and aromatic hydrocarbons, aliphatic alcohols, chloroform, diethyl aether, aliphatic ester, ketone	(70)
polycyanuric acid (nylon-1)	H_2SO_4 (95%); partially soluble in dimethyl formamide, dimethyl sulfoxide, and water	HCOOH, hexahydrophenol, cyclohexanone, phenols	(70)
poly-e-caprolactone	acetone, aromatic hydrocarbons, ethyl acetate, ethylene dichloride, tetrachloroethane, carbon tetrachloride	aliphatic hydrocarbons, ethanol	(70)
poly(maleic acid anhydride)	acetone, methyl ethyl ketone, acetophenone, dioxane, dimethyl formamide, acetonitrile, nitromethane, acetic anhydride, tetrahydrofuran, methanol, ethanol, methyl acetate, ethyl acetate, chlorinated hydrocarbons	aliphatic, cycloaliphatic, and aromatic hydrocarbons, diethyl aether, benzene, toluene, CCl_4	(38,56,57, 76)

(Continued)

Table 1. ***(Continued)***

Polymer	Solvent	Non-solvent	References
amylopectin	water, ethylenediamine, dimethyl sulfoxide	diethyl ether, acetone, ethanol, *t*-butanol	(58,77)
amylomaize	dimethyl sulfoxide, water (hot), aqueous solutions of acetic acid (pH<5), of formamide, KCl, or KOH; 1:1-mixtures of N-ethylpyridinium chloride, and pyridine respectively dimethyl formamide respectively dimethyl sulfoxide respectively sulfolane; ethylene	methanol, ethanol, butanol, hexahydrophenol, diethyl ether	(58,77)
dextran	formamide, water		(70)
polyacrylic acid (atactic)	methanol, ethanol, dioxane, ethylene glycol, dimethyl formamide, b-methoxyethanol, water, formamide, aqueous NaOH (salification)	aliphatic, and aromatic hydrocarbons, ester (methyl acetate), ketones (acetone, methyl ethyl ketone), dioxane at high temperature (swelling)	(78)
poly(vinyl acetate)	benzene, toluene, halogenated aliphatic, and aromatic hydrocarbons, methyl, ethyl, and butyl acetate, acetone, methyl ethyl ketone, 4-methyl-2-pentanone, methanol, allyl alcohol, tetrahydrofuran, dioxane, glacial acetic acid, dimethyl formamide, dimethyl	aliphatic, and cycoaliphatic hydrocarbons, ethylbenzene, xylol, CCl_4 (swelling), hexyl, and octyl acetate (swelling), amyl alcohol (swelling), diisobutyl ketone (swelling), hexanol (swelling), diethyl ether, ethanol anhydrous (swelling), diols, triols, H	(58)
polybutadiene	as polyisobutylene	as polyisobutylene	(70)
polyisobutylene	aliphatic, aromatic, and cycloaliphatic hydrocarbons (eg, heptane, diisobutylene, toluene, tetrahydronaphthalene), chlorinated aliphatic, aromatic, and cycloaliphatic hydrocarbons (eg, chloroform, CCl_4, dichlorobenzene), tetrahydrofuran, dioxane	lower ketones (acetone), lower alcohols (methanol), lower esters (methyl acetate), and lower organic acids (acetic acid), nitromethane, propionitrile	(70)

in the course of this decline in G, they represent equilibrium phases as can be seen from the common tangent to the curve at these points, which indicates the equality of the chemical potentials of the components in the coexisting phases; the distance between them determines the length of the tie line. The open circles denote points of inflection for which the second derivative of G becomes zero, they are called spinodal concentrations; between them the homogeneous mixtures are unstable, ie, even the slightest fluctuation in composition will immediately lead to phase separation. In contrast to that situation the homogeneous mixtures are metastable within the composition intervals fixed by the full circle and by the open circles; under such conditions the molecularly dispersed state may persist for any time. The limiting case of "complete immiscibility" of two components also falls into the present category; the compositions of the coexisting phases are merely shifted towards the pure components.

Curve (iii) represents a very special situation, namely critical conditions under which the tie lines degenerate into a point; in Fig. 1 the full and the empty circles coincide in the half-filled circle. Under these circumstances the second and the third derivative of $\bar{\bar{G}}$ with respect to composition become zero

$$\left(\frac{\partial^2 \bar{\bar{G}}}{\partial \varphi^2}\right)_{T,p} = \left(\frac{\partial^3 \bar{\bar{G}}}{\partial \varphi^3}\right)_{T,p} = 0 \tag{5}$$

The phenomenological thermodynamics of mixing a crystalline polymer with a liquid low molecular weight solvent is discussed by means of Fig. 2. Prior to the transfer of the polymer into the dissolved state it is necessary to melt it; this process implies an increase of the Gibbs energy of the pure polymer as indicated in the graph. The dependence of $\bar{\bar{G}}/RT$ on φ may then look similar to curve (i) of Fig. 1. Under such conditions it is, however, possible to lower the Gibbs energy of the *hypothetically* molecularly disperse mixture – within a certain compositing range – by segregating a solid phase of pure polymer. The composition at which the tangent to the curve passes the Gibbs energy of the crystalline polymer marks the saturation concentration, i.e. the equality of the chemical potential of the polymer in solutions with that in the pure crystalline state. Stable homogeneous mixtures are only formed up to the composition indicated by the full circle; beyond it, pure polymer crystals coexist with the saturated solution. The occurrence of liquid/liquid phase separation and liquid/solid phase separation at the same time, as shown later in Fig. 6 for nitrobenzene, can be rationalized by changing the shape of the curve for the homogeneous liquid mixture in Fig. 2 to case (ii) of Fig. 1.

All results presented so far refer to mixtures of two components; analogous considerations hold true for multinary systems where the possibilities for graphical representation fail if number of components becomes larger than three. For ternary systems the tangents of the binary mixtures become tangential planes and critical points form critical lines. According the Gibbs phase law the maximum number of coexisting phases at constant pressure rises by one from three to four.

Experimental Methods

There are two obvious methods for the determination of phase diagrams depicting the solubility of polymers. In the simplest case one observes under which conditions (pressure, temperature, and composition) two or more phases coexist. The criterion used for that purpose is a meniscus separating two liquids or the existence of a liquid/solid boundary. This procedure yields maps concerning the extension of a two-phase region, it does, however, normally give coarse pictures only. More detailed information is obtained by the second option, which monitors the segregation of a second phase from a homogenous mixture. In the case of liquid/liquid demixing the measurement of light transmittance is the method of first choice. As long as the refractive indices of the coexisting liquids are sufficiently different, the onset of turbidity upon the entrance of the two-phase region (induced by changes in the variables of state) is usually large enough to allow for determination of the so called cloud point by the naked eye. With many polymer solutions it is also possible to monitor the segregation of a second phase rheologically by a more or less pronounced reduction in the viscosity of the system. The reason lies in the fact that the viscosity of such two phase mixtures is usually determined by the viscosity of the polymer lean phase, constituting the matrix phase, whereas the contribution of the more viscous (polymer rich) phase – normally the disperse phase – remains little. However, caution is required because the phase diagram obtained in this manner may differ markedly from the equilibrium behavior because of special shear effects. For polymer solutions in mixed solvents the differences in the temperatures of incipient phase separation effect may reach to almost 100 °C (6). Calorimetric (7), refractive index (8) or spectroscopic methods (9,10) are sometimes also useful to monitor the segregation of a second phase.

Procedures registering merely the onset of demixing suffer from the deficiency that the thus obtained info concerning the solubility of polymers suffices only for samples with narrow molecular weight distribution. Solely under these conditions the curve of incipient phase separation becomes identical with the coexistence curve (also called binodal curve). In the general case one of the coexisting phases lies inside and the other one outside the cloud point curve as demonstrated in Fig. 4. These differences are due to fractionation, ie, to the accumulation of low molecular weight material in the polymer lean sol phase and of high molecular weight material in the corresponding polymer rich gel phase. This feature causes the necessity to distinguish between cloud point curves and coexistence curves. Under these circumstances the coexistence curves split into two separate branches depending in their position on the particular over-all polymer concentration; only for the critical composition of the system the coexistence curve is closed; under these conditions it intersects the cloud point curve at the critical temperature and at the critical composition.

Typical Results

This section deals with two component systems only. It excludes uncommon polymers and solvents. An overview concerning the typical behavior of ternary systems is presented in the theoretical section.

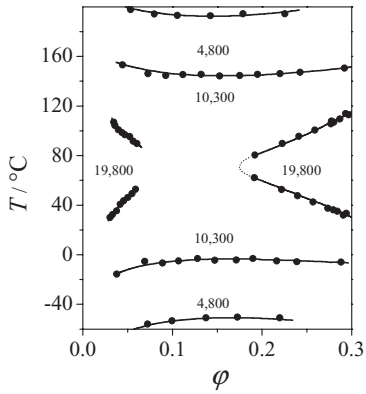

Fig. 3. Phase diagram for the system acetone/polystyrene showing both UCSTs and LCSTs (11). Molecular weights are indicated (g/mol).

Liquid/liquid Equilibria.

Influences of Temperature and Molecular Weight. Changes in the solubility of polymers can be most easily realized by increasing or decreasing the temperature. Solutions for which cooling leads to the segregation of second phase from a homogenous mixture are often addressed as UCST systems (UCST: upper critical solution temperature); LCST behavior (LCST: lower critical solution temperature) refers to the opposite case. Fig. 3 shows as an example the temperature and composition regions within which acetone can dissolve polystyrenes of different molecular weight (11). In this case the two types of miscibility gaps overlap as the molecular weight surpasses a critical value; this means that the components are at no temperature under ambient pressure completely miscible. Like with all mixtures of components differing pronouncedly in molecular weight, the extrema are shifted markedly out of the middle composition towards lower contents of the higher molecular weight material.

For low molecular weight mixtures, the compositions of coexisting phases can be immediately read from the temperature dependence of the demixing concentrations. Because polymer samples normally contain many unlike species differing in chain length or/and with respect to other properties like molecular architecture, this procedure is usually not permissible for polymer solutions and polymer mixtures. Under these circumstances a two-dimensional description of the demixing conditions represents the projection of a multidimensional situation only. Fig. 4 exemplifies this situation and demonstrates that individual coexistence curves are observed for each constant over-all composition in the case of sufficiently non-uniform polymer samples (12).

For most polymers it is possible to find good solvents; homogenous mixtures of chemically dissimilar polymers, on the other hand, are seldom. The reason lies in the low entropies of mixing, resulting from the fact that the chemical bonds between the monomeric units hinder the polymer segments to spread out over the entire volume of the system. In order to produce molecularly disperse mixtures of different macromolecules the enthalpic interactions between them should be favorable or at least neutral. Examples for complete polymer miscibility under

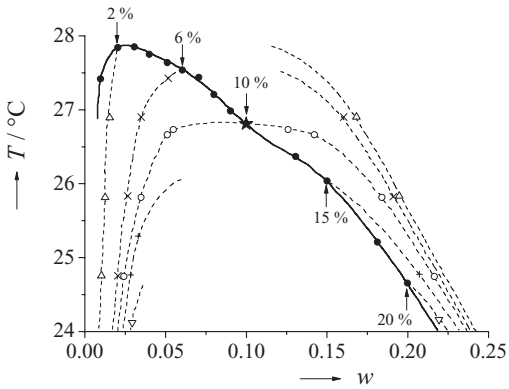

Fig. 4. Phase diagram for the solutions of a polystyrene sample with broad molecular weight distribution ($M_w = 346$ kg/mol and $M_n = 210$ kg/mol) in cyclohexane(12); w is the mass fraction of polymer. Full circles: cloud points, full line: cloud point curve, dashed lines: binodal curves (connecting the end points of the tie lines) referring to the different constant overall polymer concentrations indicated in the graph. A closed binodal curve is only observed for critical overall composition, it intersects the cloud point curve in the critical point depicted as an asterisk. Reprinted from Ref. (12), copyright 1965, with kind permission from Wiley-VCH Verlag Gmbh & Co. KGaA.

certain conditions (UCST or LCST type) are known (13), but the typical phase diagrams of polymer mixtures (often also called polymer blends) look qualitatively similar to the hour glass shaped curves shown in Fig. 3 for the higher molecular weight samples; this means that a certain minimum mutual solubility may occur at some temperature or pressure but complete miscibility can never be achieved under the experimentally accessible conditions. The extremely small mixing tendency of macromolecules becomes impressively manifest by the fact that linear and branched polymers or even oligomers made of identical monomeric units are often only incompletely miscible (14).

Pressure Influences. Elevated pressures are sometimes required in technical processes and information on their effect on the miscibility of the components is needed. Fig. 5 gives some examples(15) for the magnitude of these effects in the case of polymer solutions with either UCST or LCST behavior.

Flow Influences. In contrast to the behavior of low molecular weight mixtures, the solubility of polymers in a given solvent (16) and their miscibility with a second, chemically different polymer(17,18) can be markedly changed as the systems flow. These effects may be positive or negative, depending on the variables of state, the molecular weights of the components, the composition of the mixture plus type of flow (shear or elongational) and the corresponding shear rates or rates of strain. Shear induced mixing is, according to present knowledge, the most abundant behavior, but shear induced demixing also occurs. The effects are particularly large for ternary system (polymer solutions in a mixed solvent or polymer blends in a common solvent) where the demixing temperatures may change up to 100 °C (6). These at the first glance surprising phenomena can be rationalized by the fact that a flowing polymer solution may store energy when it flows. For the characterization of such systems this extra energy must be added

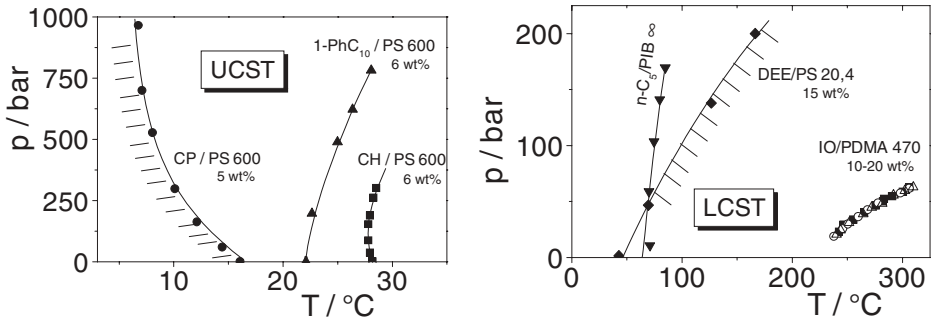

Fig. 5. Demixing pressures for polymer solutions of fixed composition (indicated at the different curves) as a function of temperature for UCST and LCST systems(15). The two phase side of the curves is hatched. PS: polystyrene, PIB: polyisobutylene, PDMA poly(n-decyl methacrylate) The numbers after the abbreviation state the molecular weight in kg/mol. CP: cyclopentane, 1-PhC_{10}: 1-phenyl decane, CH: cyclohexane, n-C_5 : n-pentane, DEE: diethylether, IO: isooctane. Reprinted from Ref. (15), copyright 1997, with kind permission from IUPAC.

to its Gibbs energy to yield a generalized Gibbs energy (19); because the stored energy varies with composition, it may alter the shape of the composition dependence of $\bar{\bar{G}}/RT$ shown in Fig. 1 and consequently change the phase behavior.

Liquid/solid Equilibria. The solubility of crystalline polymers is normally considerably lower than that of amorphous polymers because they require an additional energy, namely, the heat of fusion, in order for the bulk polymer to mix with solvent. Fig. 6 shows as an example the behavior of semi crystalline polyethylene in two different solvents (20). The solvent xylene is favorable in the temperature range of interest (no liquid/liquid demixing); up to the melting temperature $T_{m,o}$ of the pure polymer a saturated solution coexists with the crystalline polyethylene and the components are completely miscible once T has surpassed $T_{m,o}$. Nitrobenzene on the other hand, is thermodynamically less favorable and exhibits liquid/liquid demixing in addition to the solid/liquid phase separation. In this case one observes the coexistence of three phases at a characteristic temperature (broken line in Fig. 6) and concentration.

Some polymers are liquid crystalline in the pure state or dissolve to form anisotropic solutions. The most extensively studied systems of this type are solutions of polypeptides that exist in the rodlike α-helical conformation(21,22). For instance: At low temperatures poly(γ-benzyl-L-glutamate) (PBLG) and dimethylformamide are almost immiscible. However, at moderate temperatures and quite abruptly over a narrow range of temperatures, PBLG takes up considerable amounts of solvent and at higher temperatures the components are miscible for all volume fractions of polymer greater than $\varphi = 0.1$ or 0.2. This solution is ordered, owing to the constraints in packing the rod like macromolecules at these concentrations. On the other hand, at very small concentrations of polymer the macromolecules can arrange isotropically and form a single-phase solution. A very narrow gap or "chimney" of immiscibility separates the isotropic from the anisotropic region on the temperature–composition phase diagram.

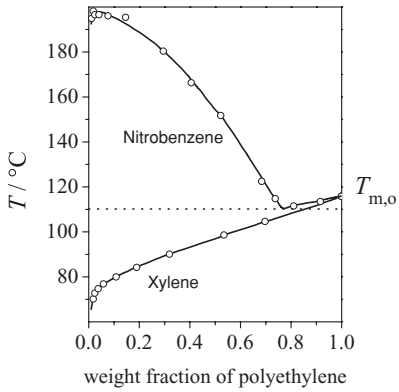

Fig. 6. Phase diagrams for polyethylene with nitrobenzene and with xylene (20); the broken line indicates the coexistence of three phases. Courtesy of the Royal Society of Chemistry.

Theory and Comparison with Experiments

Flory-Huggins Theory. The Flory-Huggins early approach enabled a basic understanding of the particularities of polymer-containing mixtures (23). It neglects volume changes upon mixing as well as some aspects of chain connectivity (leading to a very uneven distribution of polymer segments in highly dilute solutions) and the fact that the spatial extension of chain molecules may change as the composition of the mixture varies. The Flory-Huggins (24–27) model uses a combinatorial analysis to estimate the number of configurations available to the system when a flexible polymer in its disordered state mixes with the solvent. This leads to the following expression for the composition dependence of the segment molar entropy of mixing

$$\Delta \bar{\bar{S}}_{mix}^{comb} = -R\left((1-\varphi)\ln(1-\varphi) + \frac{\varphi}{N}\ln\varphi\right) \tag{6}$$

in this relation the segment fraction of the polymer is already replaced by the very similar volume fraction φ as discussed above. N is the number of the polymer segments calculated from the molar volumes of the components according to

$$N = \frac{\bar{V}_{polymer}}{\bar{V}_{solvent}} \tag{7}$$

Under the (unrealistic) assumption that eq. 6 describes the entropy part of the mixing process adequately, the expression for the segment molar Gibbs energy of mixing can be obtained by simply adding the enthalpy part of the mixing

process

$$\Delta\overline{\overline{G}} = RT\left((1-\varphi)\ln(1-\varphi)+\frac{\varphi}{N}\ln\varphi\right)+\Delta H$$
$$= RT\left((1-\varphi)\ln(1-\varphi)+\frac{\varphi}{N}\ln\varphi+\chi^*(1-\varphi)\varphi\right) \tag{8}$$

The additional presumption that the heat effects are directly proportional to the probability of contact formation between polymer segments and solvent molecules, i.e. to the product φ (1-φ), enables the introduction of the system specific parameter χ^*; in eq. 8 the parameter is given an asterisk to distinguish it from the Flory-Huggins interaction parameter χ which is in current use. The necessity for that discrimination stems from the fact the interaction parameters for real systems vary with composition. This means that the experimentally accessible χ values, obtained according to eq. 9 from chemical potentials (ie, from derivatives of the Gibbs energy with respect to composition), disagree with the χ^* values of eq. 8 (which refer to the integral Gibbs energy and are experimentally inaccessible).

$$\frac{\Delta\overline{\overline{G}}_{solvent}}{RT} = \ln(1-\varphi)+\left(1-\frac{1}{N}\right)\varphi+\chi\varphi^2 \tag{9}$$

The integral interaction parameter χ^* and the differential Flory-Huggins interaction parameter χ are interrelated by

$$\chi^* = -\frac{1}{1-\varphi}\int_1^{1-\varphi}\chi d\varphi \tag{10}$$

In spite of the simplifications specified above, the original Flory-Huggins theory is capable of reproducing many of the experimental observations at least qualitatively. Fig. 7 gives an example for this situation and shows how the measured phase diagram can be modeled, if the interaction parameters are adjusted to the maxima of the different curves (28). The results demonstrate that the original theory predicts the extension of the two-phase region by far too small. A fundamental deficiency concern the inability of the approach to deal with pressure influences (because of the assumption of zero volumes of mixing) and to explain some well documented phenomena, like multiple critical points in binary systems (29).

The Flory-Huggins theory as formulated in eq. 9 is still in common use because of its simplicity; all deviations of a real system from the combinatorial behavior formulated in eq. 6 are being incorporated into the parameter χ. This procedure implies that χ does in the general case no longer constitute an exclusively enthalpic quantity but contains an entropy contribution part too according to

$$\chi = \chi_H + \chi_S \tag{11}$$

where both constituents will normally depend on the composition of the mixture.

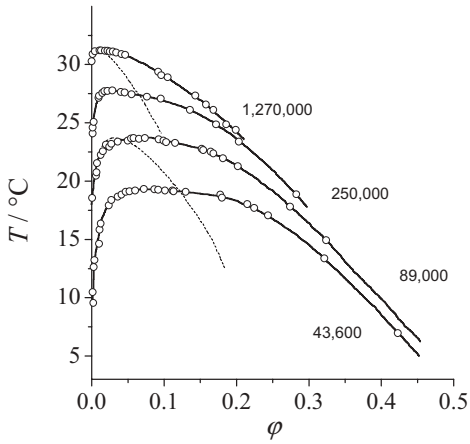

Fig. 7. Phase diagrams for four fractions of polystyrene mixed with cyclohexane plotted against the volume fraction φ of polystyrene (28). The molecular weight of each fraction is given (g/mol). The dashed lines show the predictions of the Flory-Huggins theory for two of the fractions. Courtesy of American Chemical Society.

Like with the modeling of liquid/liquid phase equilibria, the original Flory-Huggins theory was also suited to describe liquid/solid phase equilibria at least in an approximate manner. The corresponding equation applies to the freezing-point depression $\Delta T = T_{m,o} - T_m$

$$\frac{T_{m,o} - T_m}{T_m} = \left(\frac{RT_{m,o}}{\Delta \mathrm{h} \rho_{polymer} \bar{V}_{solvent}}\right)[(1-\varphi) - \chi^*(1-\varphi)^2] \tag{12}$$

Δ h is the specific heat of fusion, ρ the polymer density and $\bar{V}$ the molar volume of the solvent.

Solubility Parameter Theory. Many attempts have been made to make the Flory-Huggins theory more predictive. One of these approaches is often utilized to tackle technical problems, namely the solubility parameter theory (30,31) (SPT). It attempts to calculate the enthalpy contribution to the Flory-Huggins interaction parameter by means of a quantity known as the solubility parameter δ; it is defined as the square root of the cohesive energy density as follows

$$\delta_i = \left(\frac{\bar{E}^{vap}}{\bar{V}_i}\right)^{0.5} = \left(\frac{\bar{H}^{vap} - RT}{\bar{V}_i}\right)^{0.5} \tag{13}$$

where $\bar{E}^{vap}$ is the molar energy of vaporization and $\bar{H}^{vap}$ is the corresponding enthalpy. The solubility parameters of low molecular weight liquids are directly accessible. These cohesive energy densities range typically from 170 J/cm^{3}for neopentane, which is near the low end for organic liquids, to 1100 J/cm^{3}for glycerol, near the high end. Water, with its extensive hydrogen bonding, has an extraordinarily high cohesive energy density of 2300 J/cm^3. Several methods have been employed, most of them using a series of potential solvents to determine the solubility parameters of the polymer. The variation of the intrinsic

viscosity of the polymers with the solubility parameters of different solvents provides another access. It is also possible to estimate solubility parameters by summing group contributions (32–35). These and other procedures have been described in detail (32,33) and compiled for large numbers of polymers and solvents (34,36).

Originally the solubility parameter theory was established to study the heats of mixing for nonpolar liquids (30,31); later on it was also employed to polymer solutions. The improper assumption that the Flory-Huggins interaction parameter is exclusively of enthalpic origin yields the following simple expression

$$\chi \approx \frac{(\delta_{solvent} - \delta_{polymer})^2 \bar{V}_{solvent}}{RT} \tag{14}$$

It is obvious that this procedure is inadequate; the fact that the square of the differences of the solubility parameters can only assume positive values implies that the dissolution of polymers is always proceding exothermally in contrast to reality. Furthermore it necessarily misses the entropy parts of χ. For this reason eq (14) is often rephrased as

$$\chi = \frac{(\delta_{solvent} - \delta_{polymer})^2 \bar{V}_{solvent}}{RT} + \beta^* \tag{15}$$

where the additional, adjustable term β^* is typically on the order of 1/3 and supposed to account for this shortage. In spite of all these deficiencies, making forecasts very unreliable (cf. for instance Ref. (37)), the solubility parameter theory is still in use.

Contemporary Approaches. Numerous advanced theories have been formulated in the last decades to reproduce or even predict experimental findings for polymer containing mixtures. Most of them are particularly suitable for the description of some phenomena and special kinds of systems, but all have in common that they have lost the straightforwardness characterizing the Flory-Huggins theory. The following, incomplete collocation states some of the wider used approaches: These are the different forms of the lattice fluid and hole theories (38), the mean field lattice gas model (39), the Sanchez-Lacombe theory (40), the cell theory (41), various perturbation theories (42), the statistical-associating-fluid-theory (43) (SAFT), the perturbed-hard-sphere chain theory (44), the UNIFAC (45) and the UNIQUAC (46) models. More comprehensive reviews of the past achievements in this area and of the applicability of the different approaches are presented in the literature (47,48)

In order to rationalize several hitherto unconceivable experimental findings and to maintain the straightforwardness of the original Flory-Huggins theory, an attempt has been made to eliminate the deficiencies, described earlier. A synopsis of the ideas underlying the approach and its application to binary and ternary polymer containing systems has recently been presented (49). For polymer solutions in single solvents this treatment yields the following expression (50) for the interaction parameter χ, as introduced in eq. 9.

$$\chi = \frac{\alpha}{(1 - \nu\varphi)^2} - \zeta(\lambda + 2(1 - \lambda)\varphi) \tag{16}$$

The parameter α corresponds to the original Flory-Huggins interaction parameter and ν accounts for the unlike surfaces of different segments with identical volumes. These dissimilarities, which are due to the particular shapes of the different types of segments (51), need to be taken into consideration because they determine how many neighbors are affected by the insertion of a further molecule to a mixture of given composition. Deviations in the entropy of mixing (at constant volume of the system) caused by this particularity are also contained in ν.

It is the second term of eq. 16, which accounts for the hitherto disregarded features. The parameter ζ quantifies the changes in the conformation of the components (primarily of the macromolecules) as a consequence of alterations in the composition of the mixtures. In thermodynamically good solvents this effect manifests itself by an increase in the size of polymer coils upon dilution; in this case $\zeta > 0$. As opposed to good solvents the coils shrink upon dilution if the solvent quality falls below a characteristic value, i.e. $\zeta < 0$. Only for theta conditions (usually determined by the condition of zero second osmotic virial coefficients) ζ becomes zero and the second term vanishes. A further feature that requires an additional parameter is chain connectivity; λ is introduced to account for the fact that the segments of a given polymer molecule cannot spread out over the entire volume of the system. This situation becomes particularly obvious with dilute solutions, where individual polymer coils are surrounded by a sea of pure solvent. Theoretical considerations make evident that values of λ are for truly high molecular weight polymers in all cases very close to 0.5. This finding enables the elimination of one adjustable parameter without noteworthy loss of accuracy by merging $\zeta\lambda$ into a single parameter and inserting the value 0.5 for the λ remaining inside the brackets of the second term of eq. 17. In this manner one obtains

$$\chi \approx \frac{\alpha}{(1 - \nu\varphi)^2} - \zeta\lambda(1 + 2\varphi) \tag{17}$$

This relation describes the experimental data for a great number of polymer solutions very accurately. It accounts for the fact that the Flory-Huggins interaction parameter is in the general case no longer independent of composition. It simplifies to the original expression as the parameters ν and $\zeta\lambda$ become zero.

The expression for the composition dependence of the Flory-Huggins interaction parameter formulated in eq. 17 enables the quantitative modeling of the majority of polymer. There exist, however, some cases which require additional terms because of special interactions. Aqueous solutions of some polysaccharides (52) represent one example; the reason is that some water molecules are so tightly bound to the macromolecules that the mixing entropies deviate considerably from combinatorial. The third term of eq. 18 accounts for these effects

$$\chi = \frac{\alpha}{(1 - \nu\varphi)^2} - \zeta(\lambda + 2(1 - \lambda)\varphi) + \varpi\varphi(3\varphi - 2) \tag{18}$$

by means of the additional parameter ϖ. Solutions of block copolymers (53) represent another instance for the necessity to consider special interactions. In this case the reason lies in the fact that the solute, although consisting of only one species, is made up of two different kinds of monomers interacting with each

other more or less favorably. This situation is well modeled by the parameter τ of eq. 19

$$\chi = \frac{\alpha}{(1-\nu\varphi)^2} - \zeta(\lambda + 2(1-\lambda)\varphi) + \tau\varphi^2(4\varphi - 3) \tag{19}$$

The different powers of φ in the last terms of eqs. 18 and 19 result from the fact that two segments are involved in the minimization of the Gibbs energy via thermodynamically preferred contacts in case of water/polysaccharide, whereas approximately three are required in the case of block copolymers.

All expressions formulated for the composition dependence of the Flory-Huggins interaction parameter simplify in the limit of high dilution ($\varphi \to 0$) to yield

$$\chi_o = \alpha - \zeta\lambda \tag{20}$$

This feature enables a very accurate determination of the sum of these parameters from measured second osmotic virial coefficients A_2 according to the relation

$$\chi_o = \frac{1}{2} - A_2\rho^2_{polymer}\bar{V}_{solvent} \tag{21}$$

For the modeling it also very helpful that the parameters α and $\zeta\lambda$ are – as expected from the theoretical considerations – not independent of each other but interrelated by an equation of the form

$$\zeta\lambda = E(2\alpha - 1) \tag{22}$$

in which E is a constant for a given type of systems typically on the order of 0.7.

In spite of the fact that the present approach is capable of modeling all available experimental information quantitatively it is not predictive for such systems. The possibilities to forecast phase diagrams for ternary systems are markedly better. In the cases studied so far it is possible to obtain at least a qualitative picture, if thermodynamic information on the three binary sub-systems is available as demonstrated by the occurrence of islands of immiscibility for solutions of two compatible polymers in a solvent which is favorable for both solutes (54). The following section collects the equations required for that purpose and discusses the phenomena that are typical for ternary mixtures (55), ie, polymer solutions in mixed solvents and for solutions of two chemically different polymers in a common solvent.

In the case of binary systems it suffices to account for binary interaction parameters as a function of composition; with ternary systems (segments of type 1, 2, and 3) the situation becomes more complicated because the thermodynamic contributions of 1/2, 1/3 and 2/3 contacts may be modified by the presence of segments of third type in their molecular vicinity. In order to allow for this feature, we subdivide the Gibbs energy of mixing into three contributions as formulated

in the following equation

$$\Delta\overline{\overline{G}} = \Delta\overline{\overline{G}}^{com} + \Delta\overline{\overline{G}}_{bin}^{res} + \Delta\overline{\overline{G}}_{ter}^{res} \tag{23}$$

The first term stands for the combinatorial effects again. The second term quantifies the contributions of stemming exclusively from binary contacts and the third term collects all effects caused by the presence of the third component in the vicinity of binary contacts. For ternary mixtures the combinatorial contribution (cf. eq. 6 referring to binary mixtures) can be generalized to

$$\frac{\Delta\overline{\overline{G}}_{mix}^{com}}{RT} = \frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \frac{\varphi_3}{N_3}\ln\varphi_3 \tag{24}$$

The following equation holds true for the residual (noncombinatorial) contributions of the binary contacts; for its practical application it is important to make sure that the definition of a segment is the same for all three binary subsystems

$$\begin{aligned}\frac{\Delta\overline{\overline{G}}_{bin}^{res}}{RT} = & \left[\frac{\alpha_{12}}{(1-\nu_{12})(1-\nu_{12}\varphi_2(1-\varphi_3))} - \zeta_{12}(\delta_{12}+\varepsilon_{12}\varphi_2(1-\varphi_3))\right]\varphi_1\varphi_2 + \\ & \left[\frac{\alpha_{23}}{(1-\nu_{23})(1-\nu_{23}\varphi_3(1-\varphi_1))} - \zeta_{23}(\delta_{23}+\varepsilon_{23}\varphi_3(1-\varphi_1))\right]\varphi_2\varphi_3 + \\ & \left[\frac{\alpha_{31}}{(1-\nu_{31})(1-\nu_{31}\varphi_1(1-\varphi_2))} - \zeta_{31}(\delta_{31}+\varepsilon_{31}\varphi_1(1-\varphi_2))\right]\varphi_3\varphi_1\end{aligned} \tag{25}$$

The parameters occurring in the above equation differ from that of eq. 17 formulated for polymer solutions) in order to cover polymer blends too. This change is necessary to account for the fact that *both* components of a polymer blend suffer from the restrictions of chain connectivity. For polymer solutions

$$\delta = 1 \qquad \text{and} \qquad \varepsilon = (1-\lambda) \tag{26}$$

The corresponding relations for polymer blends read

$$\delta = \frac{2a+b}{3} \qquad \text{and} \qquad \varepsilon = \frac{b-a}{3} \tag{27}$$

where the values of the parameters a and b are calculated along the same route as with parameter λ.

The contributions of ternary contacts between the segments of type 1, 2, and 3 to the residual Gibbs energy of mixing are quantified by means of the following

expression

$$\frac{\overline{\overline{\Delta G_{ter}}}^{res}}{RT} = -\left[(t_1 + t_{11}\varphi_1)(1-\varphi_1) + (t_2 + t_{22}\varphi_2)(1-\varphi_2) + (t_3 + t_{33}\varphi_3)(1-\varphi_3)\right]\varphi_1\,\varphi_2\,\varphi_3 \tag{28}$$

The ternary interaction parameters t_1, t_2 and t_3 measure the effects resulting from the presence of an alien segment in the molecular vicinity of a given binary intersegmental contact. For instance, t_1 quantifies changes in the interaction between segments of type 1 and 2 (as compared with the binary mixture) caused by a neighboring type 3 segment. The parameters t_{11}, t_{22} and t_{33} account for the possibility that these environmental contributions may depend on the over all composition of the system. Ternary interaction parameters are normally only required for components with selectively interacting sites; in such cases they are usually indispensible for quantitative description.

The following diagrams model the complete phenomenology of phase diagrams (49,55) for polymer solutions in mixed solvents. To this end all ternary interaction parameters were set zero and the number of characteristic parameters was limited to a maximum of two for each binary system. Nevertheless all experimental observations made with ternary systems are reproduced realistically.

Fig. 8 depicts examples for the so called simplicity (ie, for a gradual transition in the solvent quality from component 1 of the mixed solvent to component 2). This calculation accounts for the differences in the size of the solvent components in terms of their numbers N of segments and assumes that they mix in a combinatorial manner. For these calculations the number of polymer segments is set equal to 1000 and their interaction with the components 1 and 2 is quantified by the corresponding values of χ_o and ν, using eqs. 17 and 22, where E = 0.7.

The solubility of polymers in mixed solvents deviates considerably from the behavior or simplicity discussed so far in most cases. Sometimes it is so pronounced that mixed solvents consisting of a mixture of two non-solvents may dissolve the polymer irrespective of its weight fraction (co-solvency). The first instance of this behavior was reported for polystyrene and mixtures of acetone plus diethyl ether (56) in the early seventies of the last century. In contrast to co-solvency, a mixed solvent consisting of two components which are both completely miscible with the polymer may lead to the establishment of two phase regions (co-non-solvency). The first such observation (57), termed co-non-solvency, was also made with polystyrene but this time the mixed solvent contained *N*,*N*-dimethylformamide plus cyclohexane. Meanwhile numerous further examples have been reported for both phenomena. Their explanation lies in the minimization of the Gibbs energy of the ternary systems. In the typical examples for *co-solvency* an additional reduction is made possible by avoiding unfavorable interactions between the components of the mixed solvent via the insertion of polymer segments between them, i.e. by homogenization. *Co-non-solvency* can in many cases be explained in terms of particularly favorable interactions of each component of the mixed solvent with the polymer as compared with the more or less "neutral" interactions between them. Under these conditions it is possible to

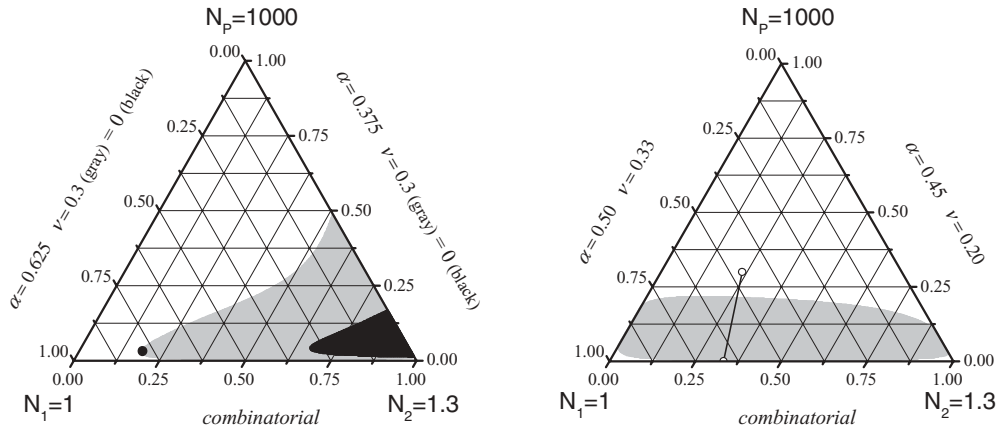

Fig. 8. Solubility of polymers in mixed solvents: *Simplicity*. These phase diagrams were calculated by means of the eqs. 23–25 in combination with eq. 22, setting E = 0.7 and λ = 0.5; furthermore it was assumed that the low molecular weight liquids mix combinatorial. The numbers of segments of the components are stated at the corners and the binary interaction parameters are indicated at the edges of the Gibbs phase triangle. The composition areas within which homogeneous mixtures are unstable (spinodal regime) are displayed in gray or black. The full circle shows a critical point; some compositions of coexisting phases are represented by open circles.

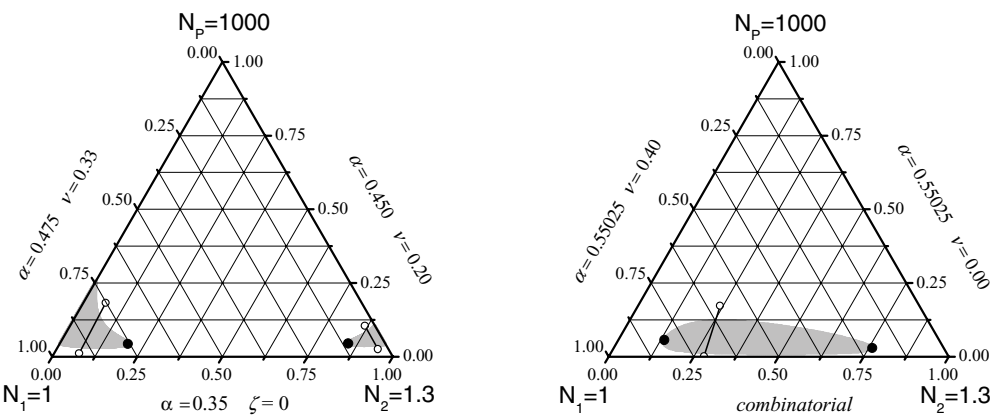

Fig. 9. Modeling by analogy to Fig. 8 but for the cases of *co-solvency* (left) and *co-non-solvency* (right). Reprinted from Ref. (49), copyright 2010, with kind permission from Springer-Science-Business Media.

lower the Gibbs energy of the total system by phase separation leading to a maximization of the highly favorable polymer solvent contacts in the polymer rich phase. Fig. 9 exemplifies these phenomena on the basis of model calculations.

So far only polymer solutions in mixed solvents have been discussed. The phenomenology is very similar for solution of two polymers in a common solvent. Again one observes simplicity and extreme deviations from it. The two most important possibilities are shown in Fig. 10.

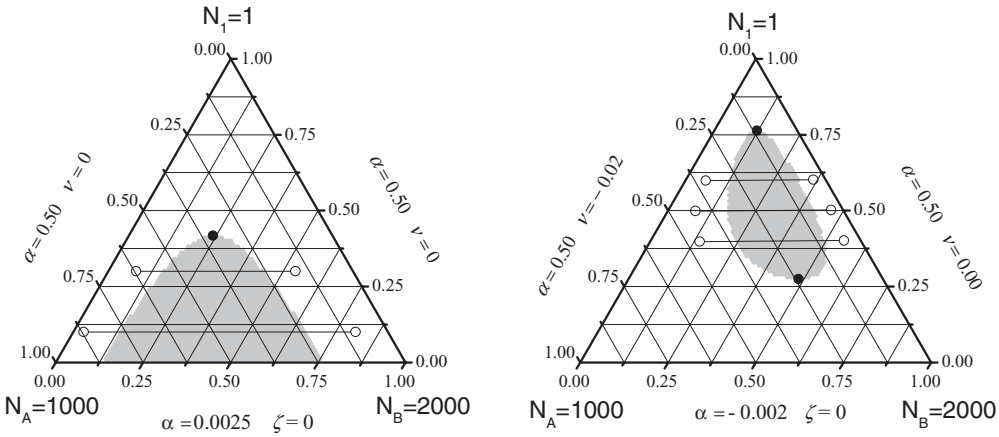

Fig. 10. Modeling of phase diagrams for solutions of the polymers A and B in a common solvent by analogy the procedure described for polymer solutions in mixed solvents. *Simplicity* (left) and *con-non-solvency* (right). Reprinted from Ref. (55), copyright 2009, with kind permission from Wiley-VCH Verlag Gmbh & Co. KGaA.

The continuous disappearance of a solubility gap existing for two incompatible polymers upon the addition of the solvent to the mixture (left side Fig. 10, displays one possibility for simplistic behavior. The example shown on the right hand side is less expected but experimentally confirmed and of great practical importance: Even systems consisting of compatible polymers, which are both completely miscible with the solvent, might exhibit a large island of immiscibility. This example for co-non-solvency is caused by the high preference of polymer/solvent contacts over contacts between the segments of the different polymers (even if they are interacting favorably). Under these circumstances the system can lower its Gibbs energy as compared with the homogeneous mixture by forming two liquid phases, one preferentially containing polymer A and the other polymer B. This procedure reduces the number of A-B contacts (associated with lower entropies of mixing than the corresponding 1-A and 1-B contacts) and increases the number of the more favorable contacts between polymer segments and solvent.

Data Summary

Solubility. Table 1 gives the information of greatest practical importance, namely whether a certain polymer mixes unlimitedly with a given liquid or not under ambient conditions. Table 2 specifies this information by stating the upper or/and lower critical solutions temperatures for systems, which are homogenous only within a certain temperature range but phase separate upon heating or cooling.

Quantitative information concerning the thermodynamic interaction between polymers and solvents is presently available for a limited number of systems only but particularly helpful to predict the solubility of polymers in mixed

Table 2. Systems Which Phase Separate upon Cooling (UCST) or/and upon Heating (LCST)

Polymer	LM	Mn/kg/mol	Mw/kg/mol	PDI	$\omega_{\text{Polymer, crit.}}$	T/K	T_{UCST}/T_{LCST}	phase behavior	Reference
PPG	water		421*				1.763	closed loop	(79)
PEG	water		2180*				1.091	closed loop	(79)
PEG	water		3350*				1.212	closed loop	(79)
PEG	water		8000*				1.397	closed loop	(79)
PEG	water		2290*				1.165	closed loop	(79)
PEG	water		3.35	1.6	0.15	518.15		UCST	(80)
					0.15	428.15		LCST	(80)
PEG	water		8	1.6	0.1	558.15		UCST	(80)
					0.1	398.15		LCST	(80)
PEG	water		15	1.2	0.075	568.15		UCST	(80)
					0.075	393.15		LCST	(80)
PS	t-butylacetate		600	1.06	0.025	278.15		UCST	(80)
					0.025	388.15		LCST	(80)
PS	t-butylacetate		233	1.06	0.075	268.15		UCST	(80)
					0.075	403.15		LCST	(80)
PS	t-butylacetate		100	1.06	0.1	253.15		UCST	(80)
					0.1	423.15		LCST	(80)
PS	ethylacetate		100	1.06	0.1	437.15		LCST	(80)
PS	ethylacetate		233	1.06	0.05	426.15		LCST	(80)
PS	ethylacetate		600	1.1	0.025	420.15		LCST	(80)
PS	methylacetate		770	1.04	0.018	305.15		UCST	(80)
					0.018	398.15		LCST	(80)
P[NIPAM-co-(N-hydroxylmethyl acrylamide)]	water					313.65		LCST	(81)

PNIPAM	water					304.15	LCST	(82)
PVME	water	4.05		1.1		310.15	LCST	(83)
PVME	D_2O				0.8	240	UCST	(84)
PVME	D_2O		20	2.5	0.6	302.85	LCST	(85)
PEO	water	83	90	1.08	$\varphi_{crit} = 0.08$	283.15	UCST	(86)
P(EOEOVE)	water		21.9	1.33	c=0.2 g/cm^3	313.65	LCST	(87)
P(EOEOVE)	water		30.4	1.26	c=0.2 g/cm^3	313.55	LCST	(87)
PNIPA	water	83.3	124	1.5	0.52	299.95	LCST	(88)
PNIPA	water	2.2	10	4.6	0.51	300.55	LCST	(88)
PNIPA	water	36	53	1.4	0.5	299.65	LCST	(88)
Poly(MOVE)	water	20		1.11		343.15	LCST	(89)
Poly(EOVE)	water	22		1.13		293.15	LCST	(89)
PVME	D_2O		20	2.5	0.6	302.85	LCST	(85)
PVME-OH	water	4.74		1.23	0.55	309.15	LCST	(90)
PVME-OCH3	water	7.19		1.05	0.7	296.15	LCST	(90)
PVME-Br	water	6.6		1.05	0.6	283.15	LCST	(90)
PVME-H	water	6.69		1.1	0.7	297.15	LCST	(90)
PVME-H	water	2.05		1.12	0.6	297.65	LCST	(90)
PVME-H	water	25		1.25	0.7	297.15	LCST	(90)
PVCL	water		9*		0.1	311.15	LCST	(91)
PVCL	water		20*		0.075	308.65	LCST	(91)
PVCL	water		275*		0.05	302.65	LCST	(91)
PIPAAm	water		16.2	2.26	0.5	307.15	LCST	(92)
PIPAAm	water		8	2.15	0.5	309.35	LCST	(92)
PIPAAm	water		4.9	1.95	0.5	315.65	LCST	(92)
PIPAAm	water		3.3	1.66	0.5	323.65	LCST	(92)
PIPAAm	water		10.6	1.53	0.5	308.45	LCST	(92)
PIPAAm	water		3.7	1.59	0.5	316.25	LCST	(92)

(Continued)

Table 2. ***(Continued)***

Polymer 1	Mn/kg/mol	Mw/kg/mol	PDI	Blends Polymer 2	Mn/kg/mol	Mw/kg/mol	PDI	$\varphi_{\text{Polymer1,crit.}}$	$\varphi_{\text{Polymer2,crit.}}$	Tc/K	Phase behavior	Reference
iPP	47500		3.2	PE	32400		3.1			416.15	UCST	(93)
PVDF	70			PMMA	50	110	2.2	0.6	0.4	142	UCST	(94)
SAN	88.6	223	2.52	PMMA	45.6	92	2.02	0.13	0.87	420.15	LCST	(95)
PC		29.2		PCL	10			0.55	0.45	545.15	LCST	(96)
PC		29.2		PCL		40		0.4	0.6	532.15	LCST	(96)
PS	34	35.7	1.05	PVME	75	95	1.27	0.5	0.5	415	LCST	(97)
PS	62	67	1.08	PVME	75	95	1.27	0.5	0.5	402	LCST	(97)
PS	100	106	1.06	PVME	75	95	1.27	0.3	0.7	393	LCST	(97)
PS	220	233	1.06	PVME	75	95	1.27	0.2	0.8	392	LCST	(97)
PS	100	106	1.06	PVME	22	45	2.05	0.2	0.8	404	LCST	(97)
PS	100	106	1.06	PVME	38	56	1.47	0.2	0.8	400	LCST	(97)
PS	100	106	1.06	PVME	62	77	1.24	0.4	0.6	394	LCST	(97)
PS	100	106	1.06	PVME	135	152	1.13	0.3	0.7	394	LCST	(97)
PnPMA		250		PVME	11	40.9	3.7	0.5	0.5	419.15	UCST	(98)
PiPMA		100		PVME	11	40.9	3.7	0.4	0.6	426.15	UCST	(98)
PS		58.7	1.03	PalphaMS		47.7	1.04	0.5	0.5	462.15	UCST	(99)
PS		117	1.06	PVME		94.3	1.82	0.3	0.7	385.15	LCST	(99)
PS		26	2.4	MMA∗S41		25	2.2	0.5	0.5	493.15	UCST	(100)
PVME				MMA∗S28		27	1.8	0.6	0.4	393.15	LCST	(100)
SBS48				PVME	37	63	1.70	0.4	0.6	455.15	UCST	(101)
								0.1	0.9	363.15	LCST	(101)
PS				PVME	37	63	1.7		0.82	375.15	LCST	(101)
PS		582	1.11	PVME		192	2.44	0.8	0.2	373.15	LCST	(102)
PS		117	1.06	PVME		94.3	1.82	0.3	0.7	385.15	LCST	(103)
PS		230		PVME		389		0.2	0.8	423	LCST	(104)
PMMA		60		PVC		55		0.7	0.3	460	LCST	(104)
PMMI	39.6	75.9	1.92	PVDF	590	872	1.48	0.6	0.4	493.15	LCST	(105)
PMMA		10.55	1.11	PS		2.95	1.05	0.6	0.4	523.15	UCST	(106)

PMMA		4.25	1.07	PS		2.95	1.05	0.5	0.5	403.15	UCST	(106)
PMMA		4.25	1.07	PS		9.2	1.03	0.4	0.6	523.15	UCST	(106)
PMMA		2.4	1.09	PS		9.2	1.03	0.3	0.7	400.15	UCST	(106)
PMMA		4.25	1.07	Palpha-MS		6.7	1.06	0.5	0.5	433.15	LCST	(106)
PMMA		4.25	1.07	Palpha-MS		3.5	1.06	0.5	0.5	453.15	LCST	(106)
PMMA		2.4	1.09	Palpha-MS		6.7	1.06	0.4	0.6	483.15	LCST	(106)
SAN		108	2.32	PMMA		92	1.87	0.25	0.75	441.15	LCST	(107)
SAN		190	2.14	PCL		95	1.65	0.2	0.8	380.15	LCST	(107)
PC		24.7	1.48	PMMA		12.9	1.04	0.3	0.7	392.15	LCST	(108)
PC		24.7	1.48	PMMA		23.8	1.07	0.3	0.7	396.15	LCST	(108)
PC		24.7	1.48	PMMA		14.8	1.53	0.3	0.7	381.15	LCST	(108)
sPMMA		50		PLLA		152		0.8	0.2	523.15	UCST	(108)
P4MS		70		P(alpha-MS)		7.5		0.3	0.7	413.15	LCST	(109)
PMMA	52.9	130		P(ECH/EO)	245	513		0.4	0.6	423.15	LCST	(110)
PMMA	52.9	130		PEO		300		0.4	0.6	503.15	LCST	(110)
PS	100		1	PVME		44.6		0.2	0.8	393	LCST	(111)
PVME	12.1	42.6	3.52	PBzMA	19.1	51	2.67	0.67	0.33	366.15	LCST	(112)
SAM		80	2-2,5	PMMAe		120	2	0.3	0.7	465.15	LCST	(113)
PEH		112		PEB		70		0.44	0.56	419.15	UCST	(114)
PMMA	104	387	3.72	SAN	56	149	2.66	0.6	0.4	423.15	LCST	(115)
PS	35.4	53	1.49	SAN	23.7	36.4	1.54	0.5	0.5	444.15	UCST	(116)
PSD		119	1.05	PVME		99	2.13	0.2	0.8	438.15	LCST	(117)
PSH		100	1.05	PVME		99	2.13	0.25	0.75	396.15	LCST	(117)
PS		26	2.4	MMA-S		25	2.2	0.5	0.5	498.15	UCST	(100)
PVME		87	1.9	MMA-S		27	1.8	0.6	0.4	393.15	LCST	(100)
PS		180	2	PVME		99	2.13	0.3	0.7	380	LCST	(118)
PVME		389		PS		230		0.8	0.2	425	LCST	(104)
PMMA		60		PVC		55		0.7	0.3	473	LCST	(104)
PC	30.5		2.1	i-PMMA	18		4.2	0.6	0.4	485.15	LCST	(119)
PVA	93	150	1.61	PMMA	92	240	2.61	0.8	0.2	450	LCST	(120)
LCP				PMMA	92	240	2.61	0.5	0.5	445	LCST	(120)

∗ critical double point.

Table 3. System Specific Parameters for the Quantitative Thermodynamic Modeling of Binary Polymer/Solvent Systems

Polymer	Solvent	T/°C	M/kg/mol	Mw/kg/mol	Mn/kg/mol	α	ν	ζ	λ	$\zeta\lambda$	ϖ	χo	Reference
PDMS	MEK	20				0.5		0					(121)
PDMS	MEK	40				0.3		−0					(121)
PDMS	TL	40				1.1		1.1					(121)
PDMS	Oct	40				3.3		5.4					(121)
PVME	CH	35	28			1.6	0.4			1.1			(50)
PVME	CH	45	28			1.6	0.38			1.1			(50)
PVME	CH	55	28			1.5	0.38			1.1			(50)
PVME	CH	65	28			1.7	0.38			1.3			(50)
PVME	CH	35	51			1.5	0.4			1			(50)
PVME	CH	45	51			1.5	0.38			1			(50)
PVME	CH	55	51			1.5	0.38			1.1			(50)
PVME	CH	65	51			1.6	0.38			1.2			(50)
PVME	CH	35	81			1.2	0.36			0.7			(50)
PVME	CH	45	81			1.2	0.35			0.7			(50)
PVME	CH	55	81			1.2	0.34			0.8			(50)
PVME	CH	65	81			1.3	0.34			0.8			(50)
PS	CH	35	233			0.5	0.33			0			(50)
PS	CH	45	233			0.6	0.31			0.1			(50)
PS	CH	55	233			0.6	0.26			0.1			(50)
PS	CH	65	233			0.6	0.21			0.1			(50)
PS	BZ	25	234			0.6	0			0.1			(50)
PS	TL	25	90			0.6	−0.1			0.2			(50)
PS	TCM	50	290			1	0.12			0.4			(50)
PS	EB	130	275			0.1	0.14			−0.1			(50)
PDMS	MEK	40		152	87	0.6	0.39			0.1			(122)
PDMS	TL	40		152	87	0.6	0.29			0.2			(122)

PDMS	n-C8	40	152	87	0.9	0.33			0.5	(122)
PVME	CH	51			1.5	0.38			1.1	(123)
PIB	BZ	25	90		0.5	0.31			0	(123)
PIB	BZ	30			2.9	0.4			2.5	(123)
PIB	BZ	48			1.8	0.55			2.5	(123)
PIB	BZ	64			1.4	0.44			1.4	(123)
1,4-PB	n-C4	25	650	224.14	0.7	−0.3	−0			(124)
1,4-PB	n-C4	50	650	224.14	0.6	−0.5	−0			(124)
1,4-PB	n-C4	75	650	224.14	0.7	−0.8	−0			(124)
1,2-PB	n-C4	25	105	97.22	0.2	0.04	0.7			(124)
1,2-PB	n-C4	50	105	97.22	0	0.06	0.5			(124)
1,2-PB	n-C4	75	105	97.22	0.1	0.01	0.5			(124)
PS	CH	37	180	176.47	0.5				0	(125)
PS	TL	37	180	176.47	0.1				0.6	(125)
PS	TBA	110	180	176.47	0.5				0	(125)
PVME	CH	37			1.5				1	(125)
PBMA	2-POH	25			0.6				0.1	(125)
PBMA	2-POH	90			0.4				0	(125)
Solu	270		96	46.8	57	−0.6	38	0.4		(126)
Solu	500		228	82	57	−0.6	38	1.34		(126)
Borreg	1200		536	97.3	57	−0.6	38	1.36		(126)
PMMA	CHCl3	50	100	90.9	2.7	0.36			2.3	(127)
PMMA	AC	50	100	90.9	0.5	0.2			0	(127)
PMMA	MeAc	50	100	90.9	−0	0.7			−0.5	(127)
PMMA	TL	50	100	90.9	1	0.41			0.6	(127)

(Continued)

Table 3. ***(Continued)***

Polymer	Solvent	T/°C	M/kg/mol	Mw/kg/mol	Mn/kg/mol	α	ν	ζ	λ	$\zeta\lambda$	ϖ	χo	Reference
PMMA	THF	20		92	41.8	0.2	0	−0	0.5				Unpublished results
PS	CHCl3	50		94.9	89.3	0.7	0			0.2			(127)
PS	AC	50		94.9	89.3	0.5	0.34			0			(127)
PS	MeAc	50		94.9	89.3	0.3	0			−0.2			(127)
PS	TL	50		94.9	89.3	1.3	0.38			0.9			(127)
NMMO∗H2O	H2O	80				−10	0.34			−7			(128)
NMMO∗H2O	H2O	90				−20	0.3			−12			(128)
NMMO∗H2O	H2O	100				−18	0.15			−7.5			(128)
Pullulan	H2O	25		277	79.7	−0	0.82			−0.8	2.4		(52)
Pullulan	H2O	38		277	79.7	−0	0.75			−0.9	2.2		(52)
Pullulan	H2O	50		277	79.7	−1	0.59			−2	3		(52)
Dextran	H2O	25		59.5	27.8	−0	0.95			−0.5	0.8		(52)
Dextran	H2O	38		59.5	27.8	−0	0.8			−0.7	0.5		(52)
Dextran	H2O	50		59.5	27.8	−0	0.8			−0.7	1.8		(52)
Dextran	H2O	25		2100	300	−0	0.88			−0.6	1.6		(52)
Dextran	H2O	38		2100	300		0.81			−0.7	0.6		(52)
Dextran	H2O	50		2100	300	−0	0.78			−0.7	1.3		(52)
NMMO∗H2O	H2O					−10	0.34	−14	0.5				(129)
Solucell 270	H2O			96	46.8	57	−0.6	38	1.38				(129)
Solucell 400	H2O			169	66.5	57	−0.6	38	1.34				(129)
Solucell 500	H2O			228	82	57	−0.6	38	1.34				(129)

Borreg 1200	H2O			536	91.3	57	−0.6	38	1.36				(129)
Solucell 400	NMMO∗ H2O	169	66.5	−25	0.04	−6	0.5				(129)		
PVME 50	THF	20		50.5	2.6		0.26			0.7	0	0	(130)
PVME 50	THF	40		50.5	2.6		0.29			0.7	0	0	(130)
PVME 50	THF	60		50.5	2.6		0.29			0.7	0	0	(130)
PS 30	THF	20		29.8	1.1		0.32			1.3	0	0	(130)
PS 30	THF	40		29.8	1.1		0.31			1.2	0	0	(130)
PS 30	THF	60		29.8	1.1		0.3			1.1	0	0	(130)
PS 180	TL	20					0.31			0.5	0	0	(130)
PUL 280	H2O	38					0.75			0.5	2.2	0	(130)
PS	THF	20		5.97	5.8	1.7	0.32	2.5	0.5				(54)
PVME	THF	20		87	64	1.1	0.26	1.3	0.5				(54)
PVME	PS	20		87	64	−0	−0.6	0	1.5				(54)
PS	CH	55		240	133	0.5	0.26	0.2	0.5				(54)
PVME	CH	55		87	64	1.2	0.34	1.5	0.5				(54)
PVME	PS	55		87	64	−0	−0.6	0	1.5				(54)
PI lin	CH	25		23.2	21.5		0.33			0.3		0	(131)
PI lin	CH	45		23.2	21.5		0.35			0.5		0	(131)
PI lin	CH	65		23.2	21.5		0.26			0.3		0	(131)
PI br	CH	25		21.6	13.6		0.35			0.3		0	(131)
PI br	CH	45		21.6	13.6		0.35			0.4		0	(131)
PI br	CH	65		21.6	13.6		0.29			0.3		0	(131)
PVC 101	THF	20		101	43.9	1.4	0.39	2.3	0.5				Unpublished results

solvents. Table 3 collects the system specific parameters introduced in section on contemporary approaches.

Interaction Parameters. Table 3 gives the parameters for eqs 16–20 discussed in the section on contemporary approaches.

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