book review

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Collection of miscibility data and phase behavior of binary polymer blends based on styrene, 2,6-dimethyl-1,4-phenylene oxide and of their derivatives

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The aim of this book is to facilitate modeling and understanding of phase behavior phenomena in homopolymer/homopolymer, homopolymer/copolymer, and copolymer/copolymer blends based on styrene 2,6-dimethyl-1,4-phenylene oxide, and on their derivatives, using published data. The book brings a systematic collection of all available experimental data for these systems and related information about miscibility and phase behavior of binary blends. There is also a CD with a database of 54 polymer/polymer systems, which includes the following data: identification number; system type; composition code for the copolymer constituents; blend composition, miscibility data, and literature sources.

Modern process industries increasingly demand information about the properties of new materials and polymeric substances in particular. The design of processing equipment requires a thorough knowledge of key material properties, including compounds involved. This knowledge is also essential for the application and/or the final use of these materials.

Many databases, some of which are electronic, contain pure polymer properties and phase equilibrium of polymer solutions (density, solubility parameter, glass transition and melting temperatures, and solvent activity coefficients), and a significant amount of additional experimental data has been reported in literature. Yet, there is an overall paucity of available information on thermodynamic properties of polymers. The type of data for different polymer systems varies considerably in quantity, quality, and in the nature of experimental information provided, which makes tabulation of the data difficult. For example, the distribution of polymer molar mass is a key information, which is usually unavailable, even though it significantly affects liquid-liquid equilibrium (LLE). Reports on polymer/mixed solvents or polymer/polymer miscibility data, especially in the form of complete phase equilibrium measurements, are generally missing in literature. Data are often reported simply as "soluble/insoluble" or by means of "theta temperatures" (critical solution temperature at infinite polymer molar mass). Sometimes, the data from original papers cannot be easily extracted because they are presented in graphs and/or other forms, disabling straightforward interpretation.

Some handbooks and compilations contain a part of the data required, but in many cases they lack the analytical description of a needed property. However, these data are restricted to single solvent systems and often span over a wide temperature range.

This book has been written primarily with the aim to gather all available experimental data about the miscibility and phase behavior in homopolymer/homopolymer, homopolymer/copolymer, and copolymer/co-polymer blends of styrene (S) and 2,6-dimethyl-1,4-phenylene oxide (PO) derivatives. It is an extension of



authors previous work on polymer/polymer miscibility, and provides data sets with experimental LLE data for fifty four polymer systems, together with references. The data have been collected from experimental papers and summarized in Tables 1–54. The cut-off date for literature search was May 2002.

The term "miscibility" is widely used to describe multicomponent polymer blends whose behavior is similar to single-phase systems. The term does not necessarily imply mixing at a segmental level, but suggests that the level of mixing is adequate to yield the expected macroscopic properties for a single-phase material. It should also be noted that blending of polymers involves not only thermodynamic considerations but also the thermal and mechanical history of the system, which may affect the kinetics aspects associated with the achievement of equilibrium properties. Only the equilibrium thermodynamic aspect is considered in this collection.

Data interpretation

The tables are divided in three sections covering blends of different polymer types. For each blend available data have been summarized and considerations involved in its final appearance. Only original data sources have been used.

Blends of two homopolymers: The A/B type

Blends of PS with PPO oxide. Blends of polystyrene (PS) and polyphenylene oxide (PPO) are the most investigated among systems in which only two monomer species, A and B, are involved. It is the basis of a well-known commercial product Noryl[®]. It was found and later confirmed by rheological studies that PPO and atactic PS are miscible in the whole concentration range.

Chemical modifications of either PS or PPO tend to decrease their miscibility to the point where mixing is no longer possible. This has been proven by studies of blends of polymers of styrene derivatives with PS itself, or with PPO and derivatives of 2,6-dimethyl-1,4-phenylene oxide.

Blends of PS with styrene derivative homopolymers. Blends of PS with completely halogen-substituted styrene in either the *ortho* or *para* position are immiscibile. Exceptions are PS/poly(oClS) blends, for which miscibility was observed over a certain molecular mass range of poly(oClS). If a methyl group is introduced to the benzene ring of styrene at the *para* position, poly(pMeS) is miscible with PS regardless of the blend composition.

Blends of PPO with styrene derivative homopolymers. Blends of PPO with several styrene derivative polymers have extensively been investigated. A partial substitution with fluorine, chlorine, or bromine at the *para* and *ortho* position in PS leads to polymer immiscibility in blends with PPO. PPO and poly(*o*MeS) or poly(*p*MeS) are miscible over the whole composition and molecular mass ranges.

Blends of homopolymer with copolymer: The A/(B-co-C) type

The miscibility and phase behavior of polymer blends has been the subject of extensive investigations, theoretically and experimentally. Particularly systematic have been the studies on miscibility of halogen-substituted styrene copolymers at varying degrees of substitution with PS or PPO. Authors limited themselves to the general A/(B-co-C) type of homopolymer/copolymer system, which consists of the three monomer units, A, B, and C. From the practical point of view, it is interesting to note that these blends can exhibit miscibility even if none of the homopolymer constituent pairs A/B, A/C, and B/C is miscible.

Blends of two copolymers: The (A-co-B)/(A-co-B) and (A-co-B)/(C-co-D) type

Blends of SPPO. The SPPO/SPPO system is an example of a copolymer/copolymer blend with two common segments, monomer A and B. The size of domains in phase-separated blends grows with the difference in sulfonylation.

Blends of SPPO with copolymers of styrene and styrene derivatives. These blends belong to a more common type of copolymer/copolymer system, (A-co-B)/(C-co-D), which consists of the four monomer units, A, B, C, and D. It was found that these blends owe their miscibility to an intramolecular "repulsion effect" in the absence of exothermic interactions, and that the location and the width of miscibility domains depend on phenylsulfonylation and on the position of the halogen atom in the benzene ring.

Guide to tables and CD-ROM

Tables are sufficiently clear and self-explanatory. Every table has the following structure:

- System number and abbreviated names of both components
- Exact description of the component(s), including abbreviation, source-based name, structure-based name, and Chemical Abstracts Service Registry Number (CASRN)
 - State of the system
- Type of the polymer system [A/B, A/(B_{1-w} -co- C_w), (A_{1-w} -co- B_w)/(C_{1-w} -co- D_w)] with indication of (co)polymer concentration
 - Reference (literature source)
 - Experimental method of data determination
- Parameters (constant parameters for a particular polymer blend)
- Variables (experimental variables followed with experimental data)

List of systems

System No.	System
Homopolymer/homopolymer	blends
1	PS/poly(oClS)
Homopolymer/copolymer ble	nds
2	PS/poly(S-co-oBrS)
3	PS/poly(S-co-pBrS)
4–12	PS/poly(oClS-co-pClS)
13	PS/SPPO
14	PPO/poly(S-co-oFS)
15	PPO/poly(S-co-pFS)
16	PPO/poly(S-co-oClS)
17	PPO/poly(S-co-pClS)
18, 19	PPO/poly(S-co-oBrS)
20, 21	PPO/poly(S-co-pBrS)
20, 21	PPO/poly(oFS-co-oClS)
23	PPO/poly(oFS-co-pClS)
24	PPO/poly(oFS-co-pBrS)
25	PPO/poly(oFS-co-pFS)
26	PPO/poly(oClS-co-pClS)
27	Poly(oFS)/SPPO
28	Poly(pFS)/SPPO
29	Poly(pFS)/SPPO
30	Poly(pClS)/SPPO
31	Poly(pBrS)/SPPO
32	Poly(oMeS)/SPPO
33	Poly(pMeS)/SPPO
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34	SPPO/SPPO
35	Poly(S-co-oFS)/SPPO
36	Poly(S-co-pFS)/SPPO
37	Poly(S-co-oClS)/SPPO
38	Poly(S-co-pClS)/SPPO
39	Poly(S-co-oBrS)/SPPO
40	Poly(S-co-pBrS)/SPPO
41	Poly(S-co-oMeS)/SPPO
42	Poly(S-co-pMeS)/SPPO
43	Poly(oFS-co-oClS)/SPPO
44	Poly(oFS-co-pClS)/SPPO
45	Poly(pFS-co-oClS)/SPPO
46	Poly(pFS-co-pClS)/SPPO
47	Poly(oFS-co-oBrS)/SPPO
48	Poly(oFS-co-pBrS)/SPPO
49	Poly(pFS-co-oBrS)/SPPO
50	Poly(pFS-co-pBrS)/SPPO
51	Poly(oFS-co-pFS)/SPPO
52	Poly(oClS-co-pClS)/SPPO
53	Poly(oBrS-co-pBrS)/SPPO
54	Poly(oMeS-co-pMeS)/SPPO

- Figure (to illustrate locations of one or two phase regions).

The attached CD-ROM contains information from the Table section in Excel format for easier handling. After placing the CD into a reading device, it should start automatically with autorun, otherwise the database can be open by clicking on the file "index.html". The displayed menu is self-explanatory. The List of systems gives active links to 54 folders, each containing two files, namely (1) tabXX.xls (for Table XX), and (2) figXX.jpg (for Figure XX).

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