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Radivoje Vuković, Grozdana Bogdanić, Frank E. Karasz, and William J. MacKnight

Phase Behavior and Miscibility in Binary Blends Containing Polymers and Copolymers of Styrene, of 2,6-Dimethyl-1,4-Phenylene Oxide, and of Their Derivatives

Radivoje Vuković and Grozdana Bogdanić
INA-Industrija nafte, Research and Development, Zagreb, Croatia

Frank E. Karasz[a] and William J. MacKnight
Department of Polymer Science and Engineering, Conte Center for Polymer Research, University of Massachusetts, Amherst, Massachusetts 01003-4530

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This article presents a comprehensive and systematic survey of miscibility in binary mixtures of polymers and copolymers based on styrene, on 2,6-dimethyl-1,4-phenylene oxide, and on their derivatives. Certain other systems based on methacrylate, acrylonitrile, and maleic anhydride-containing polymers are also included to complete the analysis. Experimental and theoretical studies of miscibility and phase behavior of homopolymer/homopolymer, homopolymer/copolymer, and copolymer/copolymer blends are analyzed. A mean field model is employed to correlate and predict miscibility in new systems. This model is also used to account for the different phenomena governing miscibility/immiscibility behavior, with special reference to the influence of the chemical structure of the polymers. Tables containing experimental data and related details are included for 127 polymer/polymer systems; these tables also contain summaries of the binary phase behavior. Calculated segmental interaction parameters, together with the relevant references and recommended values, are also tabulated. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00103-8]

Key words: mean-field model, miscibility, polymer blends, polystyrene, styrene derivative polymers, poly(2,6-dimethyl-1,4-phenylene oxide), phenylsulfonylated poly(2,6-dimethyl-1,4phenylene oxide), segmental interaction parameters.

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[a]Author to whom correspondence should be addressed. Electronic mail: fekarasz@polysci.umass.edu

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List of Symbols and Abbreviations

M_n	number average molecular weight
M_w	weight average molecular weight
N_i	degree of polymerization of polymer i
x	volume fraction of B in copolymer $(A_{1-x}B_x)_N$
y	volume fraction of D in copolymer $(C_{1-y}D_y)_N$
T_g	glass transition temperature
Greek	
χ_{blend}	overall interaction parameter of a blend
$\chi_{\text{blend}}^{\text{crit}}$	critical value of the overall interaction parameter of a blend
χ_{ij}	interaction parameter between segments i and j
Abbreviations	
-alt-	alternating copolymer
-co-	random copolymer
DSC	differential scanning calorimetry
LCST	lower critical solution temperature
m-	*meta*
o-	*ortho*
p-	*para*
P	poly
UCST	upper critical solution temperature
Repeating units	
AMS	α-methylstyrene
AN	acrylonitrile
BMS	β-methylstyrene
BrPPO	brominated poly(2,6-dimethyl-1,4-phenylene oxide)
IS	partially iodinated styrene repeating unit in IPS
MAN	maleic anhydride
MI	maleimide
MMA	methyl methacrylate
MMI	methyl maleimide
*o*BrS	*o*-bromostyrene
*o*ClS	*o*-chlorostyrene
*o*FS	*o*-fluorostyrene
*o*MS	*o*-methylstyrene
*p*BrS	*p*-bromostyrene
*p*ClS	*p*-chlorostyrene
*p*FS	*p*-fluorostyrene
*p*MS	*p*-methylstyrene
PO	2,6-dimethyl-1,4-phenylene oxide
PhMI	phenyl maleimide
S	styrene
SPO	phenylsulfonylated 2,6-dimethyl-1,4-phenylene oxide repeating unit in SPPO
Homopolymers	
PAMS	poly(α-methylstyrene)
P(*m*ClS)	poly(*m*-chlorostyrene)
P(*m*MS)	poly(*m*-methylstyrene)
P(*o*BrS)	poly(*o*-bromostyrene)
P(*o*ClS)	poly(*o*-chlorostyrene)
P(*o*FS)	poly(*o*-fluorostyrene)
P(*o*MS)	poly(*o*-methylstyrene)
P(*p*BrS)	poly(*p*-bromostyrene)
P(*p*ClS)	poly(*p*-chlorostyrene)
P(*p*FS)	poly(*p*-fluorostyrene)
P(*p*MS)	poly(*p*-methylstyrene)
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PS	polystyrene
Copolymers	
IPS	partially iodinated PS random copolymer≡poly(S-co-IS)
P(AMS-alt-MANI)	poly(α-methylstyrene-alt-maleic anhydride)
P(AMS-alt-MI)	poly(α-methylstyrene-alt-maleimide)
P(AMS-alt-MMI)	poly(α-methylstyrene-alt-methyl maleimide)
P(AMS-alt-PhMI)	poly(α-methylstyrene-alt-phenyl maleimide)
P(BMS-alt-MAN)	poly(β-methylstyrene-alt-maleic anhydride)
P(BMS-alt-MI)	poly(β-methylstyrene-alt-maleimide)
P(BMS-alt-MMI)	poly(β-methylstyrene-alt-methyl maleimide)
P(BMS-alt-PhMI)	poly(β-methylstyrene-alt-phenyl maleimide)
P(MMA-co-AN)	poly(methyl methacrylate-co-acrylonitrile)
P(MMA-co-BMA)	poly(methyl methacrylate-co-*n*-butyl methacrylate)
P(MMA-co-MAN)	poly(methyl methacrylate-co-maleic anhydride)

P(*o*BrS-co-*p*BrS)	poly(*o*-bromostyrene-co-*p*-bromostyrene)
P(*o*ClS-co-*p*ClS)	poly(*o*-chlorostyrene-co-*p*-chlorostyrene)
P(*o*ClS-co-*o*BrS))	poly(*o*-fluorostyrene-co-*o*-bromostyrene)
P(*o*FS-co-*o*ClS)	poly(*o*-fluorostyrene-co-*o*-chlorostyrene)
P(*o*FS-co-*p*BrS)	poly(*o*-fluorostyrene-co-*p*-bromostyrene)
P(*o*FS-co-*p*ClS)	poly(*o*-fluorostyrene-co-*p*-chlorostyrene)
P(*o*FS-co-*p*FS)	poly(*o*-fluorostyrene-co-*p*-fluorostyrene)
P(*o*MS-co-*p*MS)	poly(*o*-methylstyrene-co-*p*-methylstyrene)
P(*p*FS-co-*o*BrS)	poly(*p*-fluorostyrene-co-*o*-bromostyrene)
P(*p*FS-co-*o*ClS	poly(*p*-fluorostyrene-co-*o*-chlorostyrene)
P(*p*FS-co-*p*BrS)	poly(*p*-fluorostyrene-co-*p*-bromostyrene)
P(*p*FS-co-ClS)	poly(*p*-fluorostyrene-co-*p*-chlorostyrene)
P(PhVBE-alt-MAN)	poly(phenylvinyl sec-butyl ether-alt-maleic anhydride)
P(PhVBE-alt-MMI)	poly(phenylvinyl sec-butyl ether-alt-methyl maleimide)
P(PhVBE-alt-PhMI)	poly(phenylvinyl sec-butyl ether-alt-phenyl maleimide)
P(PhVEE-alt-MAN)	poly(phenylvinyl ethyl ether-alt-maleic anhydride)
P(PhVEE-alt-MMI)	poly(phenylvinyl ethyl ether-alt-methyl maleimide)
P(PhVEE-alt-PhMI)	poly(phenylvinyl ethyl ether-alt-phenyl maleimide)
P(S-co-AMS)	poly(styrene-co-α-methylstyrene)
P(S-co-AN)	poly(styrene-co-acrylonitrile)
P(S-co-MAN)	poly(styrene-co-maleic anhydride)
P(S-co-MMA)	poly(styrene-co-methyl methacrylate)
P(S-co-*o*BrS)	poly(styrene-co-*o*-bromostyrene)
P(S-co-*o*ClS)	poly(styrene-co-*o*-chlorostyrene)
P(S-co-*o*FS)	poly(styrene-co-*o*-fluorostyrene)
P(S-co-*o*MS)	poly(styrene-co-*o*-methylstyrene)
P(S-co-*p*BrS)	poly(styrene-co-*p*-bromostyrene)
P(S-co-*p*ClS)	poly(styrene-co-*p*-chlorostyrene)
P(S-co-*p*FS)	poly(styrene-co-*p*-fluorostyrene)
P(S-co-PhMI)	poly(styrene-co-phenyl-malei mide)
P(S-co-*p*MS)	poly(styrene-co-*p*-methylstyrene)
SPPO	partially phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) random copolymer copolymer≡poly(PO-co-SPO)

1. Introduction

This contribution is an extension of our previous discussion[1] of polymer/polymer miscibility with the purpose of discussing and systematically analyzing all available data concerning miscibility and phase behavior in homopolymer/homopolymer, homopolymer/copolymer, and copolymer/copolymer blends of styrene and 2,6-dimethyl-1,4-phenylene oxide derivatives.[2–6] Certain other blends containing polymers based on methyl methacrylate, acrylonitrile, and maleic anhydride monomer units are also included to facilitate the calculation of segmental interactions between these and the styrene repeating units. To explain the experimental observations, a mean-field model[7,8] is applied.

The term miscibility has been widely used[9] to describe multicomponent polymer blends whose behavior is similar to that expected of a single-phase system. The term does not necessarily imply mixing at a segmental level but suggests that the level of such mixing is adequate to yield the macroscopic properties expected of a single-phase material. It should also be noted that mixing polymers to obtain a blend invariably involves not only thermodynamic considerations but also the thermal and mechanical histories of the system which impact the kinetic aspects associated with the attainment of equilibrium properties. In this contribution only the equilibrium thermodynamic aspect will be discussed.

2. Theoretical Model

It is generally agreed that the thermodynamic basis for the mixing of high molecular weight materials is an exothermic heat of mixing, since the entropic contribution is small in such systems. The two polymers in a binary blend may contain units capable of some type of specific interaction favoring homogeneity and/or may display repulsive intramolecular interactions between groups that likewise promote exothermic mixing. For a discussion of polymer mixture thermodynamics, one may use the Flory–Huggins relation for the free energy of mixing[10,11] as the starting point. A generalized mean-field model based on this classical relation considers both intermolecular and intramolecular interactions and presents a simple way of understanding such phenomena in a quantitative sense. Using the mean-field approach, the phase behavior of blends can be described in terms of pairwise interactions between all segments in the blends. This theory can also provide a general explanation for the effect of chemical composition on miscibility. The basic approximation embodied in such a mean-field treatment is one which ignores the local concentration fluctuations in the vicinity of individual segments.

No attempt is made here to review mean-field models in detail. For a thorough treatment of this subject numerous recent contributions are available (see, for example, Refs. 12–17). We repeat here only those considerations which have a bearing on the discussion of miscibility of polymer blends. Briefly, the mean-field model provides for the evaluation of an overall interaction parameter χ_{blend} in a group contribution framework in terms of segmental interactions, where the segments are conveniently defined as the monomer repeating units. Some arbitrariness in defining a segment is possible, but is unimportant provided that a self-consistent approach is employed. In this model a polymer molecule is assumed to consist of a number of segments, and the polymer blend is therefore regarded simply as a mixture of individual polymer segments. In the simplest case the topology of the chain is also disregarded. For the general case of mixtures of two random copolymers of the type $(A_{1-x}B_x)_{N_1}/(C_{1-y}D_y)_{N_2}$, where N_1 and N_2 are the degrees of polymerization, the χ_{blend} parameter can be expressed as a linear combination of the segmental interaction parameters χ_{ij}:

$$\chi_{\text{blend}}=(1-x)(1-y)\chi_{AC}+(1-x)y\chi_{AD}+x(1-y)\chi_{BC}+xy\chi_{BD}-x(1-x)\chi_{AB}-y(1-y)\chi_{CD}, \quad (1)$$

where x and y represent the volume fractions of B and D segments in the respective random copolymers. The definition of the individual χ_{ij} parameters is obvious from their subscript. As has been shown in detail,[12] the calculation of the χ_{ij} optimally employs volume fractions based, for example, on Bondi's van der Waals volumes.[18,19] The first four terms on the right-hand side of Eq. (1) define additive intermolecular interactions between the nonbonded component monomers in the mixture of the two copolymers, weighted according to the copolymer compositions, whereas the remaining two terms define the intramolecular interactions between the two different monomers comprising each of the copolymers, and which in certain cases can be responsible for miscibility in the system.

The standard criterion for miscibility of such blends[8] is that χ_{blend} must be less than a critical value $\chi_{\text{blend}}^{\text{crit}}$, which for monodispersed components may be written as

$$\chi_{\text{blend}}^{\text{crit}}=0.5(N_1^{-0.5}+N_2^{-0.5})^2. \quad (2)$$

The boundary between miscibility and immiscibility domains for the copolymer/copolymer system is thus described by a function expressed in terms of x and y, such that

$$f(x,y)=\chi_{\text{blend}}-\chi_{\text{blend}}^{\text{crit}}=0. \quad (3)$$

The mean-field approximation is fairly satisfactory when the mixture consists only of long chain molecules. The most noteworthy conclusion from this analysis is that a net exothermic heat of mixing promoting miscibility can be attained even when none of the individual interaction parameters between individual units are negative, i.e., favoring miscibility, provided that one or both constituents are copolymers. This means that a favorable specific interaction between the two component macromolecules may not be an absolute requirement for their miscibility. It is of course not suggested that such specific interactions do not exist in certain cases, but miscibility, as defined here, can occur in many cases where such a strong interaction mechanism is absent.

Recently,[12] this mean-field model was tested using a database collected for blends of various systems. The predictive qualities of the model were demonstrated and further suggestions about the group-contribution method were included.

3. Experimental Data—References Concerning Phase Behavior of Polymer Blends

As stated above, this study is focused on the miscibility and phase behavior in binary mixtures containing polymers and copolymers based on styrene (S), styrene derivatives, and on 2,6-dimethyl-1,4-phenylene oxide (PO) and its derivatives. Homopolymer/homopolymer, homopolymer/random copolymer, homopolymer/alternating copolymer, random copolymer/random copolymer and random copolymer/alternating copolymer blends will be considered. The polymer systems discussed, together with pertinent references, are summarized in Table 1. The effective cutoff data for the literature search was May 1997.

Various methods have been used to determine the miscibility of polymer blends. Each technique has its own standard and sensitivity. Of all the methods used, film clarity, glass transition temperature determinations, dynamic mechanical measurement, microscopy, and neutron scattering studies, were the most frequently used for obtaining information on miscibility. These techniques will not be described here. For detailed information see, for example, Refs. 20–23.

We note that the blends investigated here were prepared by precipitation from solution, unless stated otherwise. In this study glass transition temperature T_g considerations were used as the criteria of miscibility, unless otherwise mentioned. In brief, if an amorphous polymer blend displays two distinct transitions, corresponding to the T_gs of the component (co)polymers, it is immiscible. If the polymer blend shows only a single T_g, appropriate to a weight averaged value, the system is miscible unless the proximity of the component T_gs is such that this conclusion is untenable. In practice, it may happen that neither a clear-cut single or double transition is obtained. This represents a so-called intermediate situation, in which various degrees of ''partial miscibility'' are involved.

For polymer blends showing miscibility at the temperature studied (usually 473 K), phase separation behavior was usually further investigated by annealing the miscible blend at some higher temperature. The annealing procedure consists of heating a sample to the selected temperature and holding it at that temperature for a given time to permit the attainment of equilibrium. Samples were than quenched to ambient temperature, and the T_g behavior was determined by reheating.

This article is divided into separate sections covering blends of different polymer types. We treat each blend system, reviewing the more characteristic available data and describing the considerations involved in arriving at a final assessment. Only the original data sources have been used in the analysis.

TABLE 1. Summary of experimental investigations on miscibility behavior of blends

Blend	Miscibility behavior	References
PS/PPO	miscible at molecular level	24–26, 28, 30, 31, 43, 109–118
PS/BrPPO	miscible depending on degree of bromination	7, 112, 116
PS/P(*o*FS)	immiscible	32, 35, 36
PS/P(*p*FS)	immiscible	35, 36
PS/P(*o*ClS)	miscible within certain molecular weight range	32[a], 33, 34, 37[a], 51, 119
PS/P(*m*ClS)	immiscible	33
PS/P(*p*ClS)	immiscible	33, 34
PS/P(*o*BrS)	immiscible	34
PS/P(*p*BrS)	immiscible	34
PS/P(*p*MS)	miscible within certain molecular weight range	43
PS/PAMS	miscible within certain molecular weight range	40, 41, 42[a], 55, 120, 121
PS/P(S-co-*o*FS)	miscible within certain copolymer composition and molecular weight range	36, 53
PS/P(S-co-*p*FS)	miscible within certain copolymer composition range	36
PS/P(S-co-*o*BrS)	miscible within certain copolymer composition range	34, 54[a], 122
PS/P(S-co-*p*BrS)	miscible within certain copolymer composition range	34, 54[a], 122
PS/IPS	miscible depending on degree of iodination of PS	55, 56
PS/P(S-co-AMS)	miscible within certain copolymer composition range	55[a]
PS/P(*o*FS-co-*p*FS)	immiscible	34, 63
PS/P(*o*ClS-co-*p*ClS)	miscible within certain copolymer compositon range	34, 56[a], 57[a]
PS/P(*o*BrS-co-*p*BrS)	immiscible	34
PS/SPPO	miscible depending on degree of phenylsulfonylation of PPO	6, 49[a], 72
PS/P(AMS-alt-MI)	immiscible	91
PS/P(AMS-alt-MMI)	immiscible	91
PS/P(AMS-alt-PhMI)	immiscible	91
PPO/P(*o*FS)	immiscible	32, 33, 35, 36, 46, 47
	miscible within certain molecular weight range	51
PPO/P(*p*FS)	immiscible	32, 33, 35, 36, 46, 47
PPO/P(*o*ClS)	immiscible	31–33, 38, 43–45, 48
PPO/P(*m*ClS)	immiscible	33
PPO/P(*p*ClS)	immiscible	29, 31–33, 38, 42–45, 48
PPO/P(*o*BrS)	immiscible	34, 48
PPO/P(*p*BrS)	immiscible	34
PPO/P(*o*MS)	miscible	49–51
PPO/P(*p*MS)	miscible	41, 48–52
PPO/PAMS	miscible	48, 60, 123
PPO/P(S-co-*o*FS)	miscible within certain copolymer composition range	8[a], 33[a], 34–36, 47[a], 124
PPO/P(S-co-*p*FS)	miscible within certain copolymer composition range	8[a], 33[a], 34–36, 47[a], 124, 125[a]
PPO/P(S-co-*o*ClS)	miscible within certain copolymer composition range	8[a], 32, 33[a], 34, 43, 126
PPO/P(S-co-*p*ClS)	miscible within certain copolymer composition range	8[a], 29, 31[a] 32, 33[a], 42, 43, 45, 126, 127
PPO/P(S-co-*o*BrS)	miscible within certain copolymer composition range	8[a], 34, 54[a], 65, 122, 128
PPO/P(S-co-*p*BrS)	miscible within certain copolymer composition range	8[a], 34, 54[a], 65, 128
PPO/IPS	miscible depending on degree of iodination PS	56
PPO/P(S-co-*o*MS)	miscible	49–51
PPO/P(S-co-*p*MS)	miscible	49–51
PPO/P(S-co-AMS)	miscible	60, 123
PPO/P(S-co-AN)	miscible within certain copolymer	61[a]

TABLE 1. Summary of experimental investigations on miscibility behavior of blends—Continued

Blend	Miscibility behavior	References
	composition range	
PPO/P(S-co-MAN)	immiscible	90
PPO/P(S-co-MMA)	miscible within certain copolymer composition range	62
PPO/P(*o*FS-co-*o*ClS)	miscible within certain copolymer composition range	64[a], 66, 68, 129, 130
PPO/P(*o*FS-co-*p*ClS)	miscible within certain copolymer composition range	8[a], 64[a], 66, 68, 129, 130
PPO/P(*p*FS-co-*o*ClS)	immiscible	67
PPO/P(*p*FS-co-*p*ClS)	immiscible	67
PPO/P(*o*FS-co-*o*BrS)	immiscible	51, 69, 131
PPO/P(*o*FS-co-*p*BrS)	miscible within certain copolymer composition range	51, 69[a], 131
PPO/P(*p*FS-co-*o*BrS)	immiscible	51, 69, 131
PPO/P(*p*FS-co-*p*BrS)	immiscible	51, 69, 131
PPO/P(*o*FS-co-*p*FS)	miscible within certain copolymer composition range	8[a], 33[a], 34, 46, 63[a], 64[a]
PPO/P(*o*ClS-co-*p*ClS)	miscible within certain copolymer composition range	8[a], 31, 33[a], 44[a], 64[a], 126
PPO/P(*o*BrS-co-*p*BrS)	immiscible	8, 34, 65, 128
PPO/P(*o*MS-co-*p*MS)	miscible	49–51
PPO/P(*p*MS-alt-AN)	miscible within certain copolymer composition range	70
PPO/P(AMS-alt-MI)	immiscible	91
PPO/P(AMS-alt-MMI)	immiscible	91
PPO/P(AMS-alt-PhMI)	immiscible	91
PPO/P(AMS-alt-MAN)	immiscible	90
PPO/P(BMS-alt-MAN)	immiscible	99
PPO/P(BMS-alt-MMI)	immiscible	99
PPO/P(BMS-alt-PhMI)	immiscible	99
PPO/P(PhVEE-alt-MAN)	immiscible	99
PPO/P(PhVEE-alt-MMI)	immiscible	99
PPO/P(PhVEE-alt-PhMI)	immiscible	99
PPO/P(PhVBE-alt-MAN)	immiscible	99
PPO/P(PhVBE-alt-MMI)	immiscible	99
PPO/P(PhVBE-alt-PhMI)	immiscible	99
SPPO/SPPO	miscible within certain degree of sulfonylation	6[a], 72[a]
SPPO/P(*o*FS)	miscible within certain copolymer composition range	6[a], 71[a]
SPPO/P(*p*FS)	miscible within certain copolymer composition range	6[a], 71[a]
SPPO/P(*o*ClS)	immiscible	71
SPPO/P(*p*ClS)	miscible within certain copolymer composition range	71[a]
SPPO/P(*o*BrS)	immiscible	71
SPPO/P(*p*BrS)	miscible within certain copolymer composition range	71[a]
SPPO/P(*o*MS)	miscible within certain copolymer composition range	49[a]
SPPO/P(*p*MS)	miscible within certain copolymer composition range	49[a]
SPPO/P(S-co-*o*FS)	miscible within certain copolymer composition range	6[a], 72[a]
SPPO/P(S-co-*p*FS)	miscible within certain copolymer composition range	6[a], 72[a]
SPPO/P(S-co-*o*ClS)	miscible within certain copolymer composition range	83[a]
SPPO/P(S-co-*p*ClS)	miscible within certain copolymer composition range	83[a]
SPPO/P(S-co-*o*BrS)	miscible within certain copolymer composition range	84[a]
SPPO/P(S-co-*p*BrS)	miscible within certain copolymer composition range	84[a]
SPPO/P(S-co-*o*MS)	miscible within certain copolymer	49[a]

TABLE 1. Summary of experimental investigations on miscibility behavior of blends—Continued

Blend	Miscibility behavior	References
	composition range	
SPPO/P(S-co-*p*MS)	miscible within certain copolymer composition range	49
SPPO/P(S-co-AN)	miscible within certain copolymer composition range	6[a], 72[a]
SPPO/P(S-co-MAN)	miscible within certain copolymer composition range	90
SPPO/P(*o*FS-co-*o*ClS)	miscible within certain copolymer composition range	88[a]
SPPO/P(*o*FS-co-*p*ClS)	miscible within certain copolymer composition range	88[a]
SPPO/P(*p*FS-co-*o*ClS)	miscible within certain copolymer composition range	89[a]
SPPO/P(*p*FS-co-*p*ClS)	miscible within certain copolymer composition range	89[a]
SPPO/P(*o*FS-co-*o*BrS)	miscible within certain copolymer composition range	132[a]
SPPO/P(*o*FS-co-*p*BrS)	miscible within certain copolymer composition range	132[a]
SPPO/P(*p*FS-co-*o*BrS)	miscible within certain copolymer composition range	132[a]
SPPO/P(*p*FS-co-*p*BrS)	miscible within certain copolymer composition range	132[a]
SPPO/P(*o*FS-co-*p*FS)	miscible within certain copolymer composition range	85[a]
SPPO/P(*o*ClS-co-*p*ClS)	miscible within certain copolymer composition range	86[a]
SPPO/P(*o*BrS-co-*p*BrS)	miscible within certain copolymer composition range	87[a]
SPPO/P(*o*MS-co-*p*MS)	miscible within certain copolymer composition range	49
SPPO/P(AMS-alt-MAN)	miscible within certain copolymer composition range	90
SPPO/P(AMS-alt-MI)	immiscible	91
SPPO/P(AMS-alt-MMI)	miscible within certain copolymer composition range	91
SPPO/P(AMS-alt-PhMI)	miscible within certain copolymer composition range	91[a]
SPPO/P(BMS-alt-MAN)	immiscible	99
SPPO/P(BMS-alt-MMI)	immiscible	99
SPPO/P(BMS-alt-PhMI)	immiscible	99
SPPO/P(PhVEE-alt-MAN)	immiscible	99
SPPO/P(PhVEE-alt-MMI)	immiscible	99
SPPO/P(PhVEE-alt-PhMI)	miscible within certain copolymer composition range	99[a]
SPPO/P(PhVBE-alt-MAN)	immiscible	99
SPPO/P(PhVBE-alt-MMI)	immiscible	99
SPPO/P(PhVBE-alt-PhMI)	miscible within certain copolymer composition range	99
PAMS/P(S-co-AMS)	miscible within certain copolymer composition range	57[a]
PMMA/P(S-co-AN)	miscible within certain copolymer composition range	133, 134[a], 135[a]
P(S-co-AN)/P(S-co-MAN)	miscible within certain copolymer composition range	76[a]–79[a],136[a]
P(S-co-AN)/P(S-co-MMA)	miscible within certain copolymer composition range	80[a]–82[a], 107
P(S-co-AN)/P(S-co-PhMI)	miscible within certain copolymer composition range	79[a]
P(S-co-AN)/P(MMA-co-BMA)	miscible within certain copolymer composition range	137[a]
P(S-co-MMA)/P(S-co-MMA)	miscible within certain copolymer composition range	73[a]

TABLE 1. Summary of experimental investigations on miscibillity behavior of blends—Continued

Blend	Miscibility behavior	References
P(S-co-MMA)/P(S-co-MAN)	miscible within certain copolymer composition range	81[a], 136
P(S-co-MMA)/P(MMA-co-AN)	miscible within certain copolymer composition range	80[a]
P(S-co-MMA)/P(MMA-co-MAN)	miscible within certain copolymer composition range	82[a]

[a]Indicates references that also contain corresponding phase diagram.

3.1. Blends of Two Homopolymers $[A_{N_1}/B_{N_2}]$

Blends of PS with PPO. Among blends in which only two monomer species, A and B, are involved, the blend of PS and PPO represents the most highly investigated miscible system containing PS. This blend also forms the basis of the well-known commercial product carrying the trade name Noryl.[24] The earliest studies of PPO and PS blends yielded inconclusive results in that two distinct phases (PS-rich and PPO-rich phases) could be resolved from dynamic mechanical loss peak measurements.[25,26] The same samples, however, exhibited only a single T_g in differential scanning calorimetry (DSC) measurements. Further studies involving dielectric relaxation data revealed only a single T_g intermediate between those observed for the individual blend components.[27] The dielectric relaxation peaks were, however, noticeably broader than the corresponding relaxations for the pure polymers. It was concluded that while a certain level of miscibility occurred, compositional fluctuations were prevalent enough to suggest definite levels of microheterogeneity. Later, Shultz *et al.*[28,29] concluded that PPO and atactic PS are miscible at all concentration levels and attributed the reported instances of nonhomogeneity to inefficient mixing. Rheological studies by Prest and Porter[30] also indicated miscibility of the PPO/PS blend. This system also offers the possibility of more complex phase behavior by virtue of the fact that PPO can crystallize under certain conditions, while the substitution of isotactic PS for the atactic isomer yields an additional degree of freedom with respect to the crystallinity of the latter component.[31]

Chemical modifications of either PS or PPO tend to decrease miscibility in this system and can render the blend entirely immiscible when carried far enough. This can be readily established through 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 Homopolymers of Styrene Derivatives. It has been reported that blends of PS with completely halogen-substituted styrene in either the *ortho* or *para* position exhibit immiscibility.[32–36] Exceptions to this behavior concern PS/poly(oClS) blends, for which miscibility was observed over a certain molecular weight range of the poly(oClS).[32,34,37] Ryan[34] clearly pointed to the existence of both LCST and UCST behavior in blends of high molecular weight PS and poly(oClS), while blends containing PS with lower molecular weights are of the ''hourglass'' phase diagram type. He measured the enthalpies of mixing for these systems, finding them to be small and positive. These results are confirmed experimentally and theoretically by Zacharius *et al.*,[37] who indicated that these blends are sensitive to conformational entropic effects related to molecular weights of either or both constituents, and that the segmental interaction parameter $\chi_{\mathrm{S},o\mathrm{ClS}}$ is positive, but very small. It was reported by Krause[38] and later by Saeki *et al.*[39] and Cowie and McEwen[40] that for PS/poly(AMS) restricted miscibility occurs and a single phase is obtained over a limited molecular weight range. By introducing the methyl group in the benzene ring of styrene at the *para* position, i.e., poly(pMS), miscibility was observed in blends with PS[41] independently of blend composition.

Blends of PPO with Homopolymers of Styrene Derivatives. Blends of PPO with polymers of several styrene derivatives have been extensively investigated and the number of literature references concerning these polymer blends is large. Several authors[29,31,33–36,38,42–48] have demonstrated that complete substitution with fluorine, chlorine, and bromine at the *para* and *ortho* position in PS leads to polymer immiscibility in blends with PPO. PPO and poly(oMS) or poly(pMS) were found to exhibit miscibility over the whole composition and molecular weight ranges.[41,48–52]

3.2. Blends of Homopolymers with Random Copolymers

The miscibility and phase behavior of blends containing a random copolymer has been the subject of extensive investigations, theoretically as well as experimentally. Systematic investigations have been reported on the miscibility of halogen-substituted styrene copolymers of varying degrees of substitution with PS and also with PPO (see Table 1).

Two types of homopolymer/random copolymer systems will be discussed here: blends of the type $A_{N_1}/(A_{1-y}B_y)_{N_2}$ which contain a common segment, and blends of the more generalized type $A_{N_1}/(B_{1-y}C_y)_{N_2}$. The interesting, and from a practical point of view, important aspect, is that such blends can exhibit miscibility even when none of the homopolymer constituent pairs A/B, A/C, and B/C are miscible.

3.2.1. The $A_{N_1}/(A_{1-x}\text{-co-}B_x)_{N_2}$ Type

Blends of PS with Random Copolymers of Styrene and a Styrene Derivative. The PS/poly(S-co-*o*FS) system is a useful example of a homopolymer/random copolymer blend with one common segment. For this blend it was observed by Vuković *et al.*[36] that PS is miscible with a copolymer containing 49 mole % *o*FS. Recently, applying the enthalpy relaxation method (the direct T_g determination is complicated by the proximity of the respective transitions), it was shown by Salamons and ten Brinke[53] that PS is conditionally miscible with these copolymers depending on the PS molecular weight and the copolymer composition. Blends of a series of copolymers of styrene and halogen-substituted styrenes with PS have also been investigated in our laboratory and it was reported[54] that certain PS/poly[S-co-*o*(*p*)BrS] blends exhibit miscibility. It was found that copolymers containing 18 mole % or less of *p*BrS are miscible with PS. In the PS/poly(S-co-*o*BrS) system, miscibility was found for blends in which the copolymer contained 36 mole % or less of *o*BrS. It was shown that both systems are stable at annealing temperatures up to 573 K, i.e., a UCST could not have been observed. In the PS/partially iodinated PS (IPS)[55,56] blend, miscibility was found for copolymers with a degree of iodination of up to 15 mole %. Miscibility of PS with poly(S-co-AMS) samples of various compositions have been studied by Cowie *et al.*[57] to determine the limits of miscibility with respect to composition and molecular weight. It was demonstrated that the system is conditionally miscible within certain copolymer composition and molecular weight ranges.

3.2.2. The $A_{N_1}/(B_{1-x}\text{-co-}C_x)_{N_2}$ Type

Blends of PS with Random Copolymers of Two Styrene Derivatives. Among blends of PS with copolymers of styrene derivatives (see Table 1), only the PS/poly(*o*ClS-co-*p*ClS) blend has been stated to be miscible within a certain copolymer composition range, first by Ryan,[34] and later by Cimmino *et al.*[58] A miscibility window for this system was found for copolymers containing from about 68 to 98 mole % of *o*ClS at 423 K. The maximum in the miscibility window occurred at approximately 443 K and at a composition of 83 mole % *o*ClS.[59]

Blends of PPO with Random Copolymers of Styrene and a Styrene Derivative. PPO/poly[S-co-*o*(*p*)FS] blends exhibit conditional miscibility, i.e., miscibility behavior which depends on the copolymer composition. Thus copolymers of poly(S-co-*o*FS) containing 91 mole % or less of *o*FS were observed by Alexandrovich[33] and by Vuković *et al.*[47] to be miscible with PPO in all proportions. Poly(S-co-*p*FS) copolymers containing up to 56 mole % of *p*FS were also found to be miscible[47] with PPO. Two T_gs were present in blends in which the copolymer has a higher content of *p*FS. Blends of PPO/poly[S-co-*o*(*p*)ClS] were also found to be conditionally miscible. It was shown by the same authors[8,33] that PPO/poly(S-co-*o*ClS) blends are miscible if the content of *o*ClS in the copolymer is less than 77 mole %. Similarly, the PPO/poly(S-co-*p*ClS) system exhibits miscibility if the *p*ClS content in the copolymer is less than 81 mole %.[8,31,33] Blends of PPO with poly(S-co-*o*BrS) copolymers[8,54] containing 47 mole % or less *o*BrS in the copolymer do not show phase separation after annealing at temperatures up to 573 K. However, in annealing blends of PPO with the copolymer poly(S-co-*p*BrS), phase separation for blends containing 54 mole % or more *p*BrS was observed. For blends of PPO with partially iodinated PS, miscibility was observed for certain degrees of iodination.[56] For PPO/poly[S-co-*o*(*p*)MS] systems, miscibility was reported over the whole composition and molecular weight range by Vuković *et al.*,[49–51] while Kressler *et al.*[60] reached a similar conclusion for the PPO/poly(S-co-AMS) system.

Blends of PPO with Random Copolymers of Styrene and Acrylonitrile or Methyl Methacrylate. The phase behavior of blends of PPO with poly(S-co-AN) and its dependence on composition has been studied by means of DSC measurements and light microscopy by Kressler and Kammer.[61] In this study it was reported that blends involving copolymers containing 9.8–12.4 wt. % AN are always transparent and exhibit a single T_g. Blends of PPO with poly(S-co-MMA) random copolymers have also been studied by optical microscopy and T_g measurements by Kressler *et al.*[62] These blends were found to be miscible up to a content of 18 wt. % MMA in the copolymer, while the transition from miscibility to immiscibility was found to be independent of temperature in the 375–623 K range.

Blends of PPO with Random Copolymers of Two Styrene Derivatives. A clear example in which two polymers exhibit miscibility even when none of the respective homopolymer pairs are miscible is provided by the blend of PPO with poly(*o*FS-co-*p*FS). Thus neither poly(*o*FS) nor poly(*p*FS) is miscible with PPO, whereas a random copolymer of these two isomeric fluorostyrenes containing between 10 and 38 mole % of *p*FS is miscible with PPO (see Refs. 8, 33, 63 and 64). Miscibility between these polymer components was ascertained by the presence of a single T_g obtained by DSC, and was additionally confirmed by visual observation of the film clarity. For the corresponding chlorinated system it was found[8,33,38,64] that DSC thermograms of 50/50 wt. % blends of PPO and copolymers containing 23–64 mole % *p*ClS in poly(*o*ClS-co-*p*ClS) show a single T_g, i.e., miscibility. The quite common phenomenon of the miscibility ''window'' is well illustrated in Fig. 1, which summarizes the miscibility limits for PPO when blended with the three types of random copolymers of halogen-substituted styrenes, i.e., PPO/poly(*o*FS-co-*p*FS), PPO/poly(*o*ClS-co-*p*ClS) and PPO/poly(*o*FS-co-*p*ClS). In contrast to the fluorinated and chlorinated systems, blends of PPO and poly(*o*BrS-co-*p*BrS) are immiscible over the entire copolymer composition range, as noted by Ryan and Vuković.[34,65] Blends of poly[*o*(*p*)FS-co-*o*(*p*)ClS] and poly[*o*(*p*)FS-co-*o*(*p*)BrS] with PPO again represent systems in which none of the respective homopolymers are mutually miscible, but in which copolymers of *o*FS with *p*ClS containing 15–74 mole % *p*ClS are found to be miscible with PPO in all proportions, as reported by ten Brinke *et al.*[8] Phase behavior in

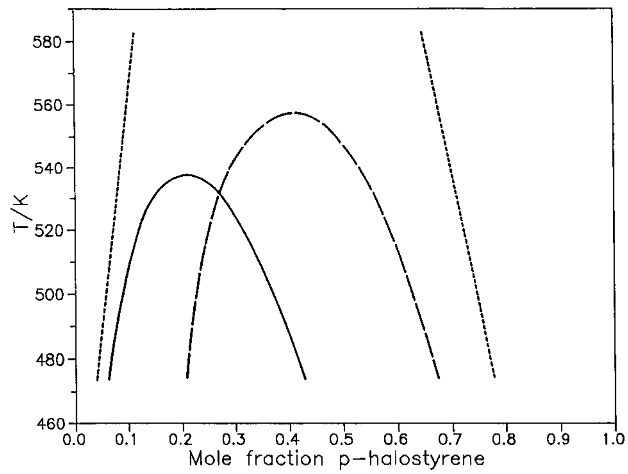

FIG. 1. Miscibility of PPO with random copolymers poly(*o*FS-co-*p*FS) (—), poly(*o*ClS-co-*p*ClS) (– –) and poly(*o*FS-co-*p*ClS) (- - -). The respective miscibility regimes lie within the conic section curves.

PPO/poly(*o*FS-co-*o*ClS) blends was investigated in our laboratory, and miscibility was observed[66,67] for blends involving copolymers containing *o*ClS between 15 and 36 mole %. We have also studied[64] the phase separation in blends of poly[*o*FS-co-*o*(*p*)ClS] with PPO at temperatures up to 593 K. Annealing the miscible blends containing *o*FS and *p*ClS comonomer units at elevated temperatures led to phase separation at 523 K only for the blend containing 74 mole % *p*ClS. Other blends did not phase separate even after annealing at higher temperatures. Miscibility and phase behavior in these two systems have been studied by Andreis *et al.*[68] using a pulsed ^{1}H-NMR (nuclear magnetic resonance) technique. The sensitivity of the method allows the detection of different separated phases on the segmental level which are not observed by the DSC method. This investigation was preceded by studying the miscibility and phase behavior of poly[*o*(*p*)FS-co-*o*(*p*)BrS] in blends with PPO.[69] Immiscibility of PPO with both homopolymers as well as with poly(*o*BrS-co-*p*BrS) was observed. Among the four copolymers poly[*o*(*p*)FS-co-*o*(*p*)BrS] blended with PPO, miscibility was observed only for PPO/poly(*o*FS-co-*p*BrS) blends in which the copolymer contains *p*BrS between 11 and 73 mole %. PPO/poly(*o*MS-co-*p*MS) blends exhibit one T_g in DSC experiments independent of blend composition, as has been reported in Refs. 49–51.

Blends of PPO with Random Copolymers of Styrene or Styrene Derivatives and Acrylonitrile. The miscibility of PPO with poly(*p*MS-co-AN) of various compositions was studied by DSC by Goh and Lim.[70] PPO is miscible with these random copolymers containing 2.7 and 5.0 wt. % of AN, but immiscible for AN contents of 7.7–26.6 wt. %. Compared to the PPO/poly(S-co-AN) blend, the onset of immiscibility in the blend occurs at a lower level of AN incorporation.

Blends of PS with Phenylsulfonylated PPO (SPPO) Copolymers. The miscibility behavior of PS with partially phenylsulfonylated PPO (SPPO), i.e., a copolymer which contains the two repeating units, PO and SPO, was first reported by Kang *et al.*[5,6] and by Vuković and co-workers.[49] The critical degree of sulfonylation for phase separation in blends of SPPO and PS was found to be 18 mole % at 553 K, when PS of 115 000 molecular weight ($M_w/M_n<1.05$) was used. In blends of polydisperse PS with SPPO,[49] miscibility was found for systems with SPPO of 28 mole % or lower degree of sulfonylation at a temperature of 503 K, or lower than 22 mole % at 593 K. By initially annealing the miscible samples at temperatures up to 593 K, phase separation was observed for such blends containing SPPO copolymers with a degree of sulfonylation from 20 to 28 mole %.

Blends of SPPO with Homopolymers of Styrene Derivatives. An extensive series of blends of SPPO with homopolymers of styrene derivatives has been studied in our laboratory.[71] For SPPO/poly(*o*FSt) and SPPO/poly(*p*FSt) blends, a window of miscibility in the temperature–copolymer composition plot was found to be a function of the degree of sulfonylation, although the relevant composition ranges were very different for the two systems. For the SPPO/poly(*o*FSt) system, miscibility was found in which the copolymer contained from 4 to 17 mole % SPO. The miscibility window in the SPPO/poly(*p*FSt) blends extended from 17 to 66 mole % of sulfonylation; whereas SPPO/poly(*o*ClSt) blends exhibited two T_gs for all SPPO samples studied. In SPPO/poly(*p*ClSt) blends, however, miscibility was observed in blends with copolymers containing more than 9 mole % SPO. No change in miscibility was observed for any of these samples by annealing at higher temperatures. In the SPPO/poly(*o*BrSt) system immiscibility was observed independent of the degree of sulfonylation of the SPPO. In SPPO/poly(*p*BrSt) blends, miscibility was displayed in samples containing copolymers with more than 12 mole % SPO. The experimental results clearly show, as will be discussed below, that the position of the halogen atom in the benzene ring in styrenic polymers is one among several important factors in determining miscibility. However, in blends of methyl-substituted styrene derivatives with SPPO copolymers, i.e., SPPO/poly(*o*MS) and SPPO/poly(*p*MS), it was found[49] that miscibility and phase behavior depend on the degree of sulfonylation of SPPO copolymers, whereas the position of the methyl group in the benzene ring has a negligible influence on miscibility. For both of these systems thermally induced phase separation was found.

3.3. Blends of Two Random Copolymers

3.3.1. The $(A_{1-x}\text{-co-}B_x)_{N_1}/(A_{1-y}\text{-co-}B_y)_{N_2}$ Type

Blends of SPPOs. The miscibility behavior of SPPO copolymers of different compositions was studied by Kang *et al.*[6,72] using DSC in conjunction with optical microscopy. The size of the domains in the phase-separated blends was found to increase as the difference in the degree of sulfonylation increased.

Blends of poly(S-co-MMA)s. The mutual miscibility of random poly(S-co-MMA)s of different compositions but constant molecular weight was studied by Kohl *et al.*[73] at room temperature and at 453 K. Miscibility was analyzed with film cast from solutions of different solvents but which may, one assumes, not be in equilibrium. The miscibility boundaries of the blends of a given copolymer poly(S_{1-x}-co-MMA_x) with a second copolymer poly(S_{1-y}-co-MMA_y) were determined for a range of values of x and y. It was shown that the widths of the miscibility windows are strongly dependent on the MMA content. The miscibility regime was found to be wider for blends in which both constituent copolymers have a high MMA content, and was markedly wider at room temperature.

3.3.2. The $(A_{1-x}\text{-co-}B_x)_{N_1}/(A_{1-y}\text{-co-}C_y)_{N_2}$ Type

Blends of poly(S-co-AN) with poly(S-co-MAN). Hall *et al.*[74] reported miscibility in blends of these two copolymers, as evidenced by a single T_g if the poly(S-co-AN) and poly(S-co-MAN) contain approximately equal amounts of styrene (in wt. %). Kato *et al.*[75] also determined miscibility in cast films by visual inspection of film clarity when the styrene contents were nearly equal (in mole %). Maruta *et al.*[76] investigated the same system using the cloud point method and an unusually long thermal annealing protocol (up to 97 h). In the same paper, the kinetics of demixing in the two-phase regime above the LCST were measured by light scattering. The same system has been investigated by Kressler *et al.*[77] using DSC and light scattering measurements. A more detailed examination of the poly(S-co-AN)/poly(S-co-MAN) system using a variety of approaches in order to quantify the thermodynamic basis for the observed phase behavior was reported by Kim, Barlow and Paul.[78] Aoki[79] studied the rheological properties of miscible poly(S-co-AN)/poly(S-co-MAN) blends and some new results that complement and extend the information provided by Hall *et al.*[74] were obtained.

Blends of poly(S-co-AN) with poly(S-co-MMA). Phase separation measurements in blends of the statistical copolymers poly(S-co-AN)/poly(S-co-MMA) were reported by Cowie and Lath.[80] Extensive miscibility in these blends was observed. The phase behavior of these blends was also studied by Kammer and co-workers,[81] who found the blends to be miscible within certain ranges of copolymer composition. Light scattering and DSC measurements showed phase separation at elevated temperatures.

Blends of poly(S-co-AN) with poly(S-co-PhMI). The miscibility of these blends was determined by measurement of their T_gs by dynamic mechanical testing.[79] It was found again that in this system blends are miscible within certain ranges of copolymer composition. The boundaries between domains of miscibility and immiscibility were shown to be two straight lines intersecting at the origin in plots in which the abscissa and ordinate represent the volume fraction compositions of the respective copolymers.

Blends of poly(S-co-MMA) with poly(S-co-MAN). The phase behavior of this blend was studied by Kammer *et al.*[81] using light scattering and DSC measurements and it was shown that the results obtained by both methods agreed fairly well. It was observed that copolymers are miscible within a certain copolymer composition range and the miscibility map was determined.

Blends of poly(S-co-MMA) with poly(MAN-co-MMA). The system was investigated by Litauszki *et al.*[82] who showed a restricted miscibility domain in the isothermal miscibility map: for MMA in poly(MMA-co-MAN) more that 90 mole % and for MMA in poly(S-co-MMA) more than 40 mole % were required for miscibility.

Blends of poly(S-co-MMA) with poly(AN-co-MMA). The phase behavior of this system was studied by Cowie and Lath[80] and it was found that miscibility is very restricted, and is limited to blends in which both constituent copolymers have a very high MMA content.

3.3.3. The $(A_{1-x}\text{-co-}B_x)_{N_1}/(C_{1-y}\text{-co-}D_y)_{N_2}$ Type

Blends of SPPO with Random Copolymers of Styrene and Styrene Derivatives. The first experimental studies of blends of this type containing two random copolymers were reported by Kang *et al.*[72] Miscibility domains for 50/50 wt. % blends of SPPO/poly[S-co-$o(p)$FS] were investigated using DSC measurements. It was pointed out that such blends are miscible as a consequence of an intramolecular ''repulsion effect'' in the absence of exothermic interactions and that the location and the width of these domains are function of the phenylsulfonylation content as well as the position of the halogen atom in the benzene ring. Results for the miscibility of blends of the random copolymers poly[S-co-$o(p)$ClS][83] and poly[S-co-$o(p)$BrS][84] with SPPO were subsequently published by Vuković and co-workers. Results reported in Refs. 72, 83 and 84 are summarized in Figs. 2 and 3, and are discussed below.

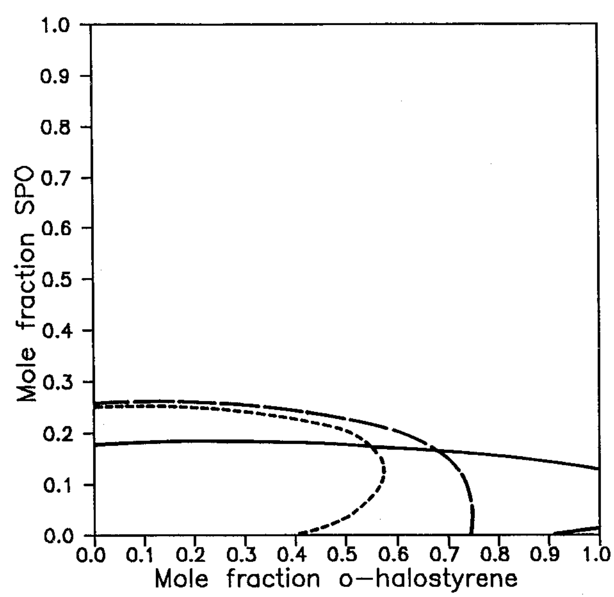

FIG. 2. Miscibility of SPPO with random copolymers poly(S-co-oFS) (—), poly(S-co-oClS) (–-) and poly(S-co-oBrS) (- - -) at 473 K. The respective miscibility regimes lie within the conic section curves.

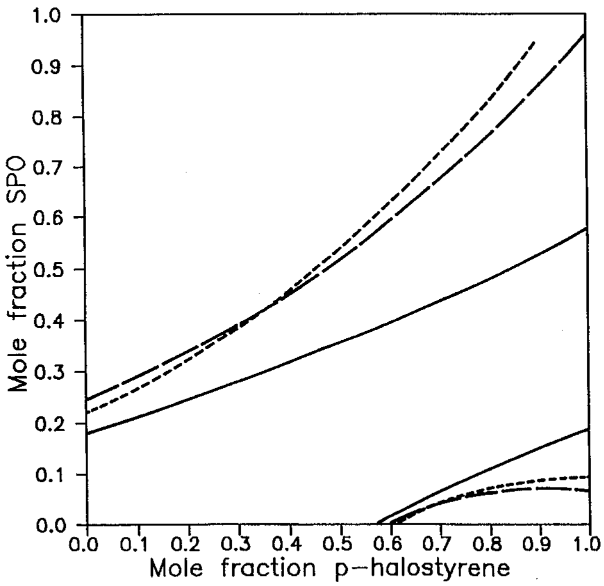

FIG. 3. Miscibility of SPPO with random copolymers poly(S-co-*p*FS) (—), poly(S-co-*o*ClS) (––) and poly(S-co-*p*BrS) (- - -) at 473 K. The respective miscibility regimes lie between the two branches of the hyperbolas.

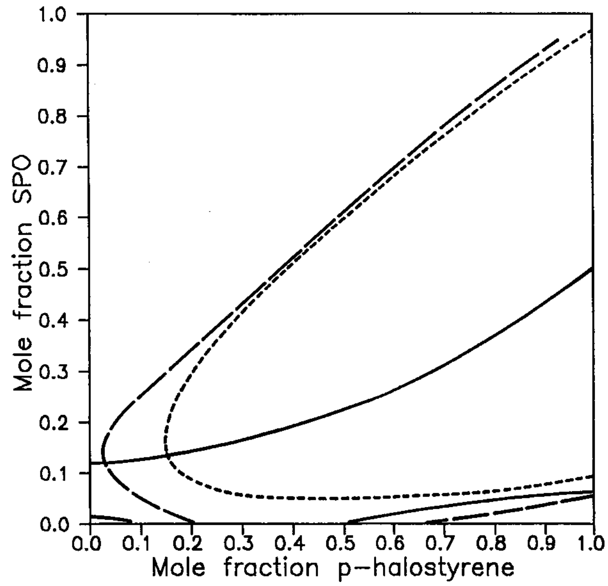

FIG. 4. Miscibility of SPPO with random copolymers poly(*o*FS-co-*p*FS) (—), poly(*o*ClS-co-*p*ClS) (––) and poly(*o*BrS-co-*p*BrS) (- - -) at 473 K. The respective miscibility regimes lie within the conic section curves.

Blends of SPPO with Random Copolymers of Different Styrene Derivatives. Miscibility of the SPPO/poly(*o*FS-co-*p*FS) system was studied by our group[85] for blends of random styrenic copolymers containing from 14 to 93 mole % *o*FSt and SPPO copolymers of various degrees of sulfonylation. The experimental miscibility boundaries were examined at several temperatures. At the higher annealing temperatures the miscibility domain became progressively smaller, indicating LCST behavior. Blends of SPPO with poly(*o*ClS-co-*p*ClS) random copolymers[86] as well as blends of SPPO with poly(*o*BrS-co-*p*BrS) random copolymers[87] exhibit conditional miscibility depending on both copolymer compositions. In these systems, upon annealing to temperatures of 553 and 593 K, only small changes in the miscibility regime were observed. A comparison of the miscibilities of these three halogenated styrene copolymers with SPPO is shown in Fig. 4. The miscibility of poly[*o*FSt-co-*o*(*p*)ClSt] copolymers with SPPO was reported in Ref. 88. It was shown above (Sec. 3.2.2) that these copolymers blended with PPO itself exhibit miscibility over certain copolymer composition ranges.[63,67] It was logical to anticipate that the phenylsulfonylated segments in SPPO copolymers will enhance miscibility in these blends, as was indeed proved by the experimental results. Miscibility was observed in systems containing SPPO copolymers with 9–87 mole % SPO blended with poly(*o*FS-co-*p*ClS) copolymers containing 10 mole % of *o*FS. At higher *o*FS content in the copolymer, the window of miscibility becomes progressively narrower. Thus, for example, for blends of the copolymer containing 85 mole % *o*FS, miscibility was observed with SPPO copolymers ranging from 3.5 to 19.4 mole % SPO content. In the SPPO/poly(*o*FS-co-*o*ClS) system, the miscibility window is consistently narrow and does not show a significant influence of the degree of sulfonylation. Copolymer blends of SPPO and poly[*p*FS-co-*o*(*p*)ClS][89] are found to be miscible for certain copolymer composition ranges, in contrast to blends of PPO itself with these systems, which are immiscible. The miscibility window for SPPO/poly(*p*FS-co-*p*ClS) is very wide and is qualitatively similar for both copolymer compositions up to 573 K. It was further found that the phase behavior is not significantly temperature dependent. A miscibility window in the system SPPO/poly(*p*FS-co-*o*ClS) is present for certain degrees of phenylsulfonylation of PPO, and becomes wider with an increase of *p*FS content in the copolymer. The window of miscibility is much narrower than in corresponding blends containing *p*ClS. Blends of SPPO copolymers with poly(*o*MS-co-*p*MS)[49] exhibited miscibility independent of the poly(*o*MeS-co-*p*MeS) copolymer composition and temperatures up to 573 K.

3.4. Blends Containing Alternating Copolymers

During the study of the polymerization of electron donor and electron acceptor monomers in the presence of free radical initiators, a large number of new alternating copolymers based on styrene, and of interest from practical and scientific points of view, were prepared in our laboratory. Since these copolymers consist of different electron donor and electron acceptor monomers, we found them potentially interesting as components in blends containing homopolymers and random copolymers related to PS and PPO. These blends are useful in any comprehensive study of the influence of chemical structure on miscibility and may also have practical applications.

The following alternating copolymers were prepared: poly(S-alt-MAN),[90] poly(AMS-alt-MAN),[90–92] poly(BMS-alt-MAN),[93] poly(AMS-alt-MI),[91,94,95] poly(AMS-alt-

MMI),[91,96,97] poly(AMS-alt-PhMI),[91,96,98] poly(BMS-alt-MMI),[99] poly(BMS-alt-PhMI),[99] poly(PhVEE-alt-MAN),[100–104] poly(PhVEE-alt-MMI),[105] poly(PhVEE-alt-PhMI),[105] poly(PhVBE-alt-MAN),[100–103,105,106] poly(PhVBE-alt-MMI)[99,105] and poly(PhVBE-alt-PhMI).[99,105] These alternating copolymers were blended with PS or PPO homopolymers as well as with random copolymers of SPPO of different degrees of sulfonylation.

3.4.1. Blends of Homopolymers with Alternating Copolymer $[A_{N_1}/(B_{1-x}\text{-alt-}C_x)_{N_2}]$

Blends with PS. In Ref. 91 we have reported that blends of the alternating copolymers poly(AMS-alt-MI), poly(AMS-alt-MMI), and poly(AMS-alt-PhMI) with PS exhibit two T_g values which are close to those of the pure components and that these systems are therefore considered immiscible.

Blends with PPO. Blends of the alternating copolymers poly(BMS-alt-MAN), poly(BMS-alt-MMI), and poly(BMS-alt-PhMI) with PPO exhibited immiscibility for all blend proportions.[99] Immiscibility was also found for blends of the alternating copolymers poly(PhVEE-alt-MAN), poly(PhVEE-alt-MMI), poly(PhVEE-alt-PhMI), poly(PhVBE-alt-MAN), poly(PhVBE-alt-MMI), and poly(PhVBE-alt-PhMI) with PPO.[99] It was observed that blends of alternating copolymers poly(AMS-alt-MI), poly(AMS-alt-MMI), and poly(AMS-alt-PhMI) with PPO show two T_g values in DSC thermograms.[91]

3.4.2. Blends of Random Copolymers with Alternating Copolymers $[(A_{1-x}\text{-co-}B_x)_{N_1}/(C_{1-y}\text{-alt-}D_y)_{N_2}]$

Blends with SPPO. The miscibility behavior of alternating copolymers poly(S-alt-MAN) and poly(AMS-alt-MAN) blended with SPPO copolymer of different degrees of phenylsulfonylation was investigated in our laboratory.[90] As for other systems discussed above, investigation of phase separation was based on DSC measurements and on film clarity. The critical degree of phenylsulfonylation of PPO for phase separation in blends of PPO with poly(S-alt-MAN) copolymers was found to be 55 mole %, i.e., blends containing a copolymer with 55 mole % or less of SPO exhibit two T_gs which are close to that of the pure components. Blends with SPPO with 64–92 mole % of SPO show only one T_g and are therefore considered miscible. In the same study, the critical degree of sulfonylation of PPO for phase separation in a SPPO/poly(AMS-alt-MAN) system was found to be 66 mole %. Further insight into the behavior of these blends was obtained by preparing samples with different blend compositions. In both systems miscibility was found to be independent of blend composition.

We have also investigated the miscibility of the alternating copolymers of AMS and several maleimides (MI, MMI and PhMI) blended with SPPO.[91] It was found that miscibility in these blends depends on the chemical structure of the blend components. Thus SPPO/poly(AMS-alt-MI) blends are considered immiscible (two T_gs for all blends), whereas SPPO/poly(AMS-alt-MMI) blends showed somewhat different behavior. In these systems one T_g value was obtained in the blends containing 39–92 mole % SPO, after the first heating in the DSC. After the second run, two T_gs appeared close in value to those of the pure components. It was concluded that these blends are partially miscible and the results imply that the thermal history of these samples is highly important. In the blends of SPPO with alternating copolymers of AMS with PhMI, miscibility was found for samples containing from 39 to 92 mole % of SPO. It should be noted that for the blends with SPPOs containing 39–64 mole % of SPO, the conclusion regarding miscibility could only be based on the polymer blend clarity because of the proximity of the respective T_gs.

For SPPO blended with alternating copolymers[99] containing β-substituted styrene derivatives, the behavior of the alternating copolymers BMS with MAN, MMI, and PhMI in blends with SPPO was investigated. It was found that all these blends display immiscibility as determined by DSC. Another series of blends containing alternating copolymers with different electron donor (PhVEE or 2PhVBE) and acceptor monomers (MAN, MMI, and PhMI), blended with SPPO random copolymers, was also studied. It was found that blends of poly(PhVEE-alt-PhMI) or poly(PhVBE-alt-PhMI) are miscible with SPPO copolymers having a SPO content of more than 60 mole % and immiscible with SPPO of a lower degree of sulfonylation. High-temperature phase separation in the miscible blends was shown to be a function of the degree of sulfonylation of the SPPO and blend composition. From the data obtained for these two systems, it is evident that copolymers containing an ethyl group show miscibility over a wider range of degrees sulfonylation of the SPPO copolymer than do copolymers containing a bulky *sec*-butyl group, which reduces the copolymer's ability to form miscible blends with SPPO.

4. Calculated Segmental Interaction Parameters Data

Employing the mean-field model described in Sec. 2, it is possible to determine the individual segmental interaction parameters from the experimentally observed miscibility/immiscibility boundaries. The purpose of this section is to summarize reported values of the interaction parameters estimated by using the mean-field model together with the relevant references. This information is given in Table 2 and should be of value in further expanding general knowledge concerning polymer/polymer interactions.

In analyzing the data, we have found, as was pointed out by Nishimoto *et al.*[107] and Salamons *et al.*,[53] that in many references in which Eq. (1) has been used, the authors failed to define the basic segmental units. In our recent paper[12] χ_{ij} segmental interaction parameters reported were based on volume fraction, calculated from Bondi's van der Waals volumes,[18,19] which may be considered as the best values for the lattice occupancy. Based on the experimental miscibility/immiscibility data, 61 χ_{ij} parameters were reestimated. Remarkable agreement between experimental miscibility

TABLE 2. Segmental interaction parameters at 473 K. (Recommended values appear in bold type)

Segment pair	χ_{ij}	Reference
S,PO	−0.0986	7
	−0.1	8
	−0.043	12
	−0.043	59
S,SPO	**0.22**	12
	0.20	72
	0.385	83
S,*o*FS	0.09	8
	0.0025	12
	0.04	72
	$0.0073<\chi_{ij}<0.018$	55
S,*p*FS	0.08	8
	0.06	12
	0.08	72
S,*o*ClS	0.005	8
	0.005	12
	0.0027	58
	0.005	59
S,*p*ClS	0.09	8
	0.055	12
	0.0792	58
	0.07	59
S,*o*BrS	**0.013**	12
	0.007	84
S,*p*BrS	0.2	7
	0.048	12
	0.051	84
S,*p*IS	**0.09**	12
	0.09	56
S,*o*MS	**0.0025**	12
S,*p*MS	**0.003**	12
S,AMS	0.032	40
	0.003	57
	0.032	60
S,MAN	**1.85**	12
	1.85	79
	0.34	81
S,MMA	**0.04**	12
	0.03	80
	0.01	81
	0.02	107
	0.31	133
	0.0044	138
	0.0376	139
S,AN	**0.98**	12
	0.17	61
	0.7	72
	0.98	79
	0.829	80
	0.12	81
	0.744	107
	2.13	133
	0.899	140[a]
S,PhMI	**0.29**	12
	0.29	79
PO,SPO	**0.25**	12
	0.318	71
	0.15	72
PO,*o*FS	0.013	8
	0.005	12
	0.005	71
	0.004	72
PO,*p*FS	0.09	8
	0.057	12
	0.037	71
	0.053	72
PO,*o*ClS	0.03	8
	0.021	12
	0.02	59
PO,*p*ClS	0.045	8
	0.034	12
	0.03	59
PO,*o*BrS	**0.047**	12
	0.029	71
PO,*p*BrS	0.2215	7
	0.055	12
	0.044	69
	0.035	71
PO,*p*IS	**0.097**	12
	0.097	56
PO,*o*MS	**0.006**	12
PO,*p*MS	**0.005**	12
	0.005	48
	0.005	52
PO,AMS	**0.11**	12
	0.024	91
PO,MMA	**0.21**	12
	0.54	62
PO,AN	**1.23**	12
	0.5	61
	0.96	70
	0.745	72
PO,MAN	**1.68**	12
	0.355	90
PO,PhMI	**0.9**	12
	0.038	91
SPO,*o*FS	**0.176**	12
	0.252	71
	0.113	72
SPO,*p*FS	**0.046**	12
	0.093	71
	0.022	72
SPO,*o*ClS	**0.175**	12
	0.28	71

TABLE 2. Segmental interaction parameters at 473 K—Continued

Segment pair	χ_{ij}	Reference
SPO,*p*ClS	**0.009**	12
	0.017	71
SPO,*o*BrS	**0.15**	12
	0.270	87
SPO,*p*BrS	**0.01**	12
	0.013	71
SPO,*o*MS	**0.18**	12
	0.137	49
SPO,*p*MS	**0.17**	12
	0.13	49
SPO,AMS	**0.505**	12
	0.015	91
SPO,AN	**0.2**	12
	0.097	72
SPO,MAN	**0.81**	12
	0.006	90
SPO,PhMI	**0.39**	12
	0.006	91
*o*FS,*p*FS	0.17	8
	0.04	12
	0.058	85
*o*FS,*o*ClS	**0.064**	12
	0.032	88
*o*FS,*p*ClS	**0.07**	12
	0.068	88
*o*FS,*o*BrS	**0.042**	12
	0.033	132
*o*FS,*p*BrS	**0.108**	12
	0.171	69
	0.057	132
*p*FS,*o*ClS	**0.11**	12
	0.083	89
*p*FS,*p*ClS	**0.043**	12
	0.052	89
*p*FS,*o*BrS	**0.12**	12
	0.091	132
*p*FS,*p*BrS	**0.11**	12
	0.082	132
*o*ClS,*p*ClS	0.16	8
	0.09	12
	0.094	58
	0.10	59
*o*BrS,*p*BrS	**0.1**	12
	0.065	87
*o*MS,*p*MS	**0.01**	12
*p*MS,AN	**0.91**	12
	0.91	141
AMS,MAN	**1.52**	12
	0.135	90
AMS,PhMI	**1.22**	12
	0.04	91
MMA,AN	**0.5**	12
	0.461	80
	0.05	81
	0.45	107
	0.66	133
MMA,MAN	**1.2**	12
	0.20	81
AN,MAN	**0.04**	12
	0.04	71
AN,MAN	**0.04**	12
	0.04	71
	0.03	81
	−0.042	140[a]
AN,PhMI	**0.07**	12
	0.07	79

[a] χ_{ij} parameter was calculated from B_{ij} as: $\chi_{ij} = B_{ij} V_{\mathrm{ref}}/RT$, where $V_{\mathrm{ref}} = 106\ \mathrm{cm}^3/\mathrm{mol}$ according to Ref. 142.

boundaries and the boundaries calculated using the mean-field model and the revised parameters was found. Table 2 presents the χ_{ij} parameters as published in the earlier literature and also the new (recalculated) values (bold type) as presented in Ref. 12. Without hesitation, we recommend the use of the revised χ_{ij} parameters.

5. Concluding Remarks

From the experimental data presented in Sec. 3, the influence of chemical structure on the miscibility and phase behavior in blends containing polymers based on styrene and 2,6-dimethyl-1,4-phenylene oxide and their derivatives is obvious. While presenting the results of the experimental studies we have also commented on these effects qualitatively. This section is therefore limited to a few additional points: the influence of temperature, the so-called ''internal repulsion effect,'' the effects induced by the position of halogen substituents on the aromatic ring in styrene derivatives as well as the nature of these substituents. This last conclusion is based on the phase diagrams presented in Figs. 1–5.

The influence of temperature greatly depends on the tem-

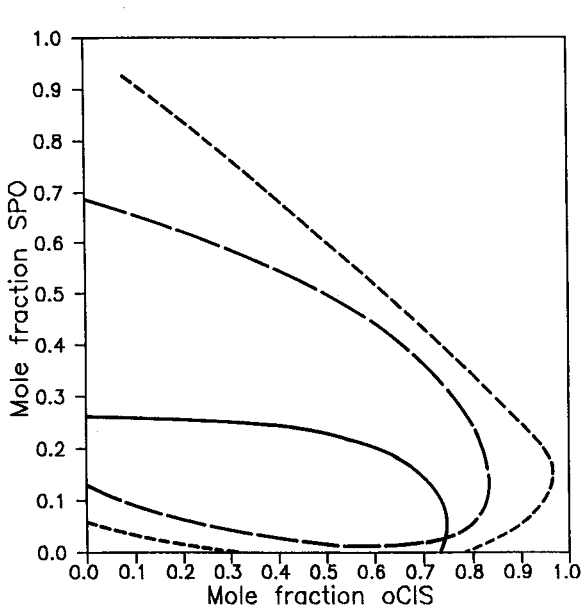

FIG. 5. Miscibility of SPPO with random copolymers poly(S-co-*o*ClS) (—), poly(*p*FS-co-*o*ClS) (– –) and poly(*p*ClS-co-*o*ClS) (- - -) at 473 K. The respective miscibility regimes lie within the conic section curves.

perature range and on the system, as is clearly shown in Fig. 1. It can be seen that around 530 K, large variations of miscibility are induced by small temperature changes for poly(*o*FS-co-*p*FS) blended with PPO, whereas variations of miscibility will be small for PPO/poly(*o*FS-co-*p*ClS) blends. At the same time, miscibility in the PPO/poly(*o*FS-co-*o*ClS) blends essentially does not change[64] by raising the temperature independently of the copolymer composition.

Figure 1 also illustrates the ''intramolecular repulsion effect,'' initially pointed out by ten Brinke *et al.*[8] and more recently, in the context of vapor–liquid equilibria, by Gupta and Prausnitz.[108] It is evident that PPO is not miscible with poly(*o*FS) or with poly(*p*FS). However, miscibility occurs in poly(*o*FS-co-*p*FS), where the *ortho* and *para* substitutions are included in the copolymer structure. The same observation can be made for the two other blends presented in Fig. 1, i.e., poly(*o*ClS-co-*p*ClS) and poly(*o*FS-co-*p*ClS). This effect is not limited to the substituted styrene copolymers; it was also observed for the SPPO, which can be regarded as the copolymer of PO and SPO units. As shown in Fig. 3, PPO and highly sulfonylated SPPO are not miscible with poly(*p*FS), but miscibility occurs for SPPOs containing between 15 and 50 mole % SPO. In this and the other two cases [SPPO/poly(S-co-*p*ClS) and SPPO/poly(S-co-*p*BrS)], partial sulfonylation acts as a promoter of miscibility. The interpretation of an intramolecular repulsion effect between different units in a copolymer arises from the mean-field approach; it sometimes involves, as in the poly(*o*FS-co-*p*FS) copolymer example, repulsion between units which differ only in terms of substituent position (e.g., *o*FS or *p*FS).

The influence of the position of the halogen substituent in the aromatic ring in styrene derivatives is demonstrated in Figs. 2, 3, and 4. Figures 2 and 3 are relevant to the blends SPPO/poly(S-co-XS) where X is a fluoro, chloro, or bromo substituent in the *ortho* position (Fig. 2) or in the *para* position (Fig. 3). The differences are obvious, and it may be concluded that *ortho* substitution is a strong inhibitor of miscibility in these systems. A similar observation arises from consideration of Fig. 4, which shows how miscibility increases in blends of SPPO with poly(*o*XS-co-*p*XS) when the amount of *para* substitution increases. This can be explained, partially at least, as a result of a steric hindrance. However it is not correct to limit the explanation to geometric considerations: for example, the van der Waals volumes of the chloro (or bromo) and the methyl groups are similar, but the location of the methyl substitution does not greatly modify miscibility.

The effect of the type of halogen on miscibility should be considered, taking into account the simultaneous influence of the volume of the substituent, of its electronegativity, and of its position in the aromatic ring. All these effects have a significant influence on miscibility. This is shown in Fig. 5, which presents the isothermal miscibility maps of blends of SPPO with the three copolymers poly(S-co-*o*ClS), poly(*p*FS-co-*o*ClS), and poly(*p*ClS-co-*o*ClS). In these examples, the *o*Cl monomer unit is common to all three copolymers. By changing the other monomer unit (to S or *p*F or *p*Cl) the miscibility domain is expanded. Taking into account other data presented in Sec. 3, we may conclude that the power of the halogen substituent and of styrene to enhance miscibility is given by *p*ClS>*p*FS>S. However, when the substituent is in the *ortho* position, the ''steric hindrance'' factor is predominant, as is shown in Fig. 2.

We will not extend our discussion here to the application of the mean-field model beyond that presented in Sec. 2, or to the consistency of interaction parameters (see Table 2) with the experimental behavior and the influences that we have already discussed (in some cases very large disagreements in χ_{ij} are reported). Such a discussion has been presented in a previous paper[12] and shows that the revised interaction parameters, which give a quantitative account of a very large amount of experimental data in condensed form, are not only physically significant but also have predictive qualities.

In the large family of blends that we described here there is still the possibility of creating new formulations. It is certainly much less expensive to perform computer experiments before preparative efforts, and the basic aim of group-contribution models, as for example the mean-field model mentioned here, is to utilize existing phase-equilibrium data to predict the phase equilibria of systems for which no data are available. While such predictions may be used for preliminary design purposes, it must be emphasized that the mean-field model is of a semiquantitative nature only. Whenever good experimental data are available, these should be used rather than the mean-field predictions.

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