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Miscibility of α-methyl styrene copolymers—extension of the mean-field treatment for the case of two copolymers

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Abstract

An extension of the mean-field approach for the case of two statistical copolymers is described which allows the analysis of copolymer–copolymer blends of the type $A_xB_{1-x} + C_yB_{1-y}$ where the copolymer (A_xB_{1-x}) with the mole fraction of monomer A (x_A) = constant is miscible with the (C_yB_{1-y}) copolymer between $y = 1$ and a single composition limit $y = y_1$, where $y_1 > 0$. Mixtures of poly(α-methyl styrene-*co*-acrylonitrile) copolymer of azeotrope composition (28.8 wt% acrylonitrile) mixed with statistical methyl methacrylate/acrylonitrile copolymers have been studied and one-phase blends have been found with methyl methacrylate/acrylonitrile copolymers of composition up to 21 wt% acrylonitrile. Estimated segmental interaction parameters acting in the system were positive. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymer–copolymer blends; Acrylonitrile copolymers; Segmental interaction parameters

1. Introduction

There has been considerable interest recently in blends involving copolymers and especially in the problem of mapping the composition boundaries that divide miscible from immiscible behaviour [1–6]. Frequently, these boundaries are used to estimate information about the interaction parameters between monomer pairs by fitting them to the form predicted by a binary interaction model combined with the Flory–Huggins theory [1,2].

Owing to the mathematical nature of this problem, it is well known that this approach alone cannot lead to the independent determination of the interaction parameters between all of the monomer pairs involved because the fitting procedure involves more parameters than experimental information can provide. Generally, at least one parameter is taken from another source, which means that each parameter subsequently evaluated includes all of the uncertainties of this value. In this connection, the polystyrene–poly(methyl methacrylate) interaction parameter, determined by Fukuda et al. [7] using light scattering measurements in an optical θ-solvent, is mainly used for the miscibility analysis of statistical copolymers containing these monomers [4,5].

Statistical styrene/acrylonitrile (SAN) copolymers are miscible with a variety of different polymers [8]. To date, only blends of α-methyl styrene/acrylonitrile copolymer (α-MSAN) at the azeotrope composition of 28.8 wt% AN have been explored extensively [9–13]. Miscibility studies using this copolymer with different acrylonitrile contents have been published recently and miscibilities with poly(alkyl methacrylate)s, chlorinated polyethylene and poly(vinyl chloride) have been established [14–17].

The inspection of the miscibility windows for the system α-MSAN–PMMA in the literature [14,15,17] shows that only the miscibility/immiscibility boundary in the region of high acrylonitrile content can be established precisely, and this limits the determination of the segmental interaction parameters based on the α-methyl styrene component. Recently Cowie et al. [18] published a modification of the mean-field approach which allows the analysis of polymer blends with only one boundary composition limit. Its extension for the case of two statistical copolymers and the application to the blends of α-MSAN copolymers with methyl methacrylate/acrylonitrile copolymers (MAN) is presented here.

2. Materials and procedures

The MAN copolymers used were prepared by photoinitiated copolymerization in the presence of naphthalene [19]

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Table 1
Molecular characteristics of MAN copolymers

Sample	Acrylonitrile (wt%)	$M_n \times 10^{-5}$	T_g (K)	Conversion (%)
1	3.7	4.16	375	6.9
2	7.2	5.92	376	5.2
3	13.0	5.32	375	6.1
4	16.8	5.81	373	5.5
5	20.0	5.27	374	5.2
6	22.0	6.10	376	5.2
7	27.5	2.17	375	4.9

as low conversion materials, thereby keeping their chemical heterogeneity low. Molecular characteristics of the MAN copolymers are summarized in Table 1. An α-MSAN copolymer of azeotrope composition (28.8 wt% AN) was a technical product of BASF, Ludwigshafen, FRG, having $M_w = 1.52 \times 10^5$ and $T_g = 401$ K.

Films of 50/50 (w/w) composition were cast from butanone solutions in a closed box under a dry nitrogen atmosphere at room temperature. The films obtained were first dried under an infrared lamp and finally in a vacuum oven at 370 K for 4 days. The blend miscibility was characterized using the criteria that a miscible blend exhibits one T_g and can be prepared as a transparent film whereas a phase-separated blend shows the T_g for both components and the film is turbid.

The glass transition temperatures of the samples and films were determined using a Perkin–Elmer DSC-2 differential scanning calorimeter, scanning at 20 K min^{-1} and T_g was taken as the extrapolated onset of the baseline shift. Phase separation of the blends on raising the temperature was detected visually on the microscope hot stage by heating them slowly at a constant rate. The onset of turbidity was taken to be the lower critical solution temperature (LCST) of the blend.

3. Results and discussion

The segmental interaction parameters are usually determined from the composition boundaries dividing miscible from immiscible behaviour in polymer blends, which for two statistical copolymers A_xB_{1-x} and C_yD_{1-y} are expressed by the equation

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

where x, y are volume fractions, expressing the copolymer composition and χ_{ij} are the segmental interaction parameters. For infinite molecular weight polymers phase separation occurs when $f(y) = 0 = \chi_{\text{crit}}$.

Many systems have been examined where a homopolymer or copolymer is miscible with a copolymer within a certain composition "window" [1–6]. For the blends where only one miscibility limit exists Cowie et al. [18] described a mean-field approach which allows the calculation of segmental interaction parameters for such systems. Its extension for the case of two statistical copolymers goes out from Eq. (1) which is a quadratic with a minimum in χ_{blend} when

$$f'(y) = x(\chi_{\text{AC}} - \chi_{\text{AD}} - \chi_{\text{BC}} + \chi_{\text{BD}}) + (\chi_{\text{BC}} - \chi_{\text{BD}} - \chi_{\text{CD}}) + 2y\chi_{\text{CD}} = 0 \quad (2)$$

Substituting for χ_{AC} from Eq. (2) into Eq. (1) and setting $y = y_0$ to indicate the minimum gives

$$f(y)/\chi_{\text{CD}} = y^2 - 2y_0y + [x(-\chi_{\text{AB}} + \chi_{\text{AD}} + \chi_{\text{BD}} + x\chi_{\text{AB}}) + \chi_{\text{BD}}]/\chi_{\text{CD}} \quad (3)$$

The first two terms on the right-hand side of Eq. (3) are a difference of squares, i.e. $y^2 - 2y_0y = (y - y_0)^2 - y_0^2$ and as in Eq. (1), $f(y) = \chi_{\text{crit}}$ at the phase boundaries, then

$$(y - y_0)^2 = [\chi_{\text{CD}}y_0^2 - x(-\chi_{\text{AB}} + \chi_{\text{AD}} - \chi_{\text{BD}} + x\chi_{\text{AB}}) + \chi_{\text{BD}} + \chi_{\text{crit}}]/\chi_{\text{CD}} \quad (4)$$

Thus the general solutions for the limits of miscibility (y_i, $i = 1$ and 2) for copolymer A_xB_{1-x} in copolymer C_yD_{1-y} are

$$y_i = y_0 \pm \{[\chi_{\text{CD}}y_0^2 - x(-\chi_{\text{AB}} + \chi_{\text{AD}} - \chi_{\text{BD}} + x\chi_{\text{AB}}) + \chi_{\text{BD}} + \chi_{\text{crit}}]/\chi_{\text{CD}}\}^{0.5} \quad (5)$$

where, for polymers of finite molecular weights, χ_{crit} is calculated from the equation:

$$\chi_{\text{crit}} = 0.5(N_1^{0.5} + N_2^{-0.5})^2 \quad (6)$$

with N_1 and N_2 being the degrees of polymerization of the copolymer samples closest to the miscibility boundaries.

The final equation for blends of two copolymers with a common monomer B, A_xB_{1-x} and C_yB_{1-y}, where $\chi_{\text{AB}} = \chi_{\text{AD}}$ and $\chi_{\text{BD}} = 0$ reduces to

$$y_1 = y_0 \pm [(\chi_{\text{CD}}y_0^2 - x_{\text{A}}^2\chi_{\text{AB}} + \chi_{\text{crit}})/\chi_{\text{CD}}]^{0.5} \quad (7)$$

Provided y_0 and one of the χ_{ij} values are known, Eqs. (2) and (7) give a means of determining the remaining two χ_{ij} parameters in blends with one miscibility limit.

The industrial α-MSAN copolymer of azeotrope composition was blended with statistical MAN copolymers of different compositions. From these measurements a miscibility window was constructed and the phase boundary composition was established. The experimental data are summarized in Table 2 and these results show that α-MSAN copolymer of azeotrope composition forms miscible blends with MAN copolymers with composition up to 21 wt% acrylonitrile. The minimum in χ_{blend} is obtained as

Table 2
Miscibility data of the system α-MSAN copolymer–methyl methacrylate/acrylonitrile copolymers

AN content in MAN (wt%)	T_g (K)	LCST (K)
0.0	385	494
3.7	389	535
7.2	384	534
13.0	386	522
16.8	388	503
20.0	387	482
22.0	375 + 399	Turbid
27.5	372 + 401	Turbid

the maximum in the LCST data at 5 wt% AN and along with $\chi_{\text{MMA–AN}} = 0.46$ from Ref. [4], the described analysis leads to the estimated values for the acrylonitrile/α-methyl styrene and α-methyl styrene/methyl methacrylate interactions of $\chi_{\text{AN-}\alpha\text{-MS}} = 0.8$ and $\chi_{\alpha\text{-MS–MMA}} = 0.03$.

These segmental interaction parameters are also available from the published miscibility windows for the system α-MSAN–PMMA [14,15,17]. Here only the published miscibility/immiscibility boundaries in the region of high acrylonitrile contents can be established precisely and boundaries at acrylonitrile contents from 37 to 42 wt% have been found depending on the molecular weight of the copolymer samples used.

For a homopolymer A mixed with a copolymer C_yD_{1-y} the blend interaction parameter χ_{blend} is given by the following function of composition:

$$\chi_{\text{blend}} = y\chi_{\text{AC}} + (1-y)\chi_{\text{AD}} - y(1-y)\chi_{\text{CD}} \tag{8}$$

The combination of these data [14] with the established boundary composition for the blends of acrylonitrile copolymers studied (Table 2), corresponding to the miscibility of two statistical copolymers with a common monomer A_xB_{1-x} and C_yB_{1-y} where

$$\chi_{\text{blend}} = x^2\chi_{\text{AB}} + (\chi_{\text{AC}} - \chi_{\text{AB}} - \chi_{\text{BC}})xy + y^2\chi_{\text{BC}} \tag{9}$$

allows the determination of the interaction parameters of α-methyl styrene segment with the acrylonitrile and methyl methacrylate segments, respectively.

The calculation of the segmental interaction parameters is based on Eqs. (8) and (9) using the value for the acrylonitrile/methyl methacrylate interaction parameter $\chi_{\text{AN–MMA}} = 0.46$ derived elsewhere [4]. This analysis led to estimated values for the acrylonitrile/α-methyl styrene and α-methyl styrene/methyl methacrylate interactions of $\chi_{\text{AN–}\alpha\text{-MS}} = 0.87$ and $\chi_{\alpha\text{-MS–MMA}} = 0.045$.

The comparison of both results shows their close agreement, which substantiates the use of the mean-field treatment with only one boundary composition limit for the determination of segmental interaction parameters between the components in polymer blends. The only exceptions are the systems with the so-called miscibility "chimneys" in the LCST region, where the proper y_0 values cannot be determined [4].

The value of $\chi_{\text{AN–}\alpha\text{-MS}}$ is large and close to that for the acrylonitrile–styrene interaction, viz. $\chi_{\text{AN–S}} = 0.83$, which is not unreasonable as the heat of mixing of polystyrene and poly(α-methyl styrene) is small and close to being athermal [20]. The comparison with the corresponding SAN blends shows that the substitution of α-methyl styrene for styrene leads to a small increase in the repulsive interaction between the copolymer components.

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References

[1] ten Brinke G, Karasz FE, MacKnight WJ. Macromolecules 1983;16:1827.
[2] Paul DR, Barlow JW. Polymer 1984;25:487.
[3] Kammer HW. Acta Polym 1986;37:1.
[4] Cowie JMG, Lath D. Makromol Chem, Macromol Symp 1988;16:103.
[5] Nishimoto M, Keskkula H, Paul DR. Polymer 1989;30:1279.
[6] Coleman MM, Graf JF, Painter PC. Specific interactions and the miscibility of polymer blends, Lancaster: Technomic, 1991.
[7] Fukuda T, Nagata M, Inagaki H. Macromolecules 1986;19:1411.
[8] Lath D, Cowie JMG, Lathová E. Polym Bull 1992;28:361 references therein.
[9] Goh SH, Siow KSJ. Appl Polym Sci 1984;29:99.
[10] Goh SH, Lee SY, Siow KSJ. Appl Polym Sci 1986;31:2055.
[11] Goh SH. Polymer J 1990;26:1149.
[12] Goh SH, Lee SY. Polym Commun 1990;31:463.
[13] Silvestri R, Ring M, Pavan A. Macromolecules 1989;22:1402.
[14] Suess M, Kressler J, Kammer HW, Heinemann K. Polym Bull 1986;16:371.
[15] Cowie JMG, Elexpuru EM. Eur Polym J 1992;28:623.
[16] Cowie JMG, Elexpuru EM, McEwen IJ. J Polym Sci, B: Polym Phys 1991;29:407.
[17] Gan PP, Paul DR, Padwa AR. Polymer 1994;35:1487.
[18] Cowie JMG, McEwen IJ, Nadvornik L. Macromolecules 1990;23:5106.
[19] Barton J, Capek I, Lath D, Lathová E. Chem Papers 1977;31:2657.
[20] Cowie JMG, McEwen IJ. Polymer 1985;26:1662.