Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Determination of Polymer Compatibility by Viscometric Measurements on Ternary Solutions of the Two Polymers

Omar Melad[a]; James E. Mark[a]
[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA

To cite this Article Melad, Omar and Mark, James E.(2005) 'Determination of Polymer Compatibility by Viscometric Measurements on Ternary Solutions of the Two Polymers', Journal of Macromolecular Science, Part A, 42: 10, 1319 — 1327

To link to this Article: DOI: 10.1080/10601320500203918

URL: http://dx.doi.org/10.1080/10601320500203918

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:1319–1327, 2005

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320500203918

Determination of Polymer Compatibility by Viscometric Measurements on Ternary Solutions of the Two Polymers

OMAR MELAD AND JAMES E. MARK

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, USA

Results on the intrinsic viscosity [η] are reported for the system solvent(1)/polymer(2)/polymer(3) in which the solvent was benzene, polymer(2) was polystyrene (PS), and polymer(3) was poly(dimethylsiloxane) PDMS. The values of [η] were then used to determine the likely compatibility of polymer blends of PS and PDMS. Initial focus was on the traditional interaction parameter $b_{23}^{(1)}$ used by several authors to predict compatibilities, it but depends on the molar mass, weight fractions, and concentrations of each polymer. A new interaction parameter $b_{23}^{(2)}$ that is independent of polymer(3) concentration and molar mass was evaluated for determinations of polymer compatibility.

Keywords polymer-solvent, interaction parameter, polymer blend compatibility

Introduction

The investigation of polymer-polymer interactions by solution property measurements is a subject of considerable interest (1). In this approach, the viscosity behavior of polymer A (guest polymer), is determined in a solution that contains a second polymer B (host polymer) at constant concentration. It is assumed that polymer-polymer interactions in solution dominate over polymer-solvent interactions (2, 3), such as those involving the polarity or dielectric constant of the solvent (1).

There are several specific techniques used in this area (1). Dilute solution viscometry (DSV) is a particularly useful method because of its simplicity and low cost (4–11). It is based on Huggins plots of η_{sp}/C vs. C, where η_{sp} is the specific viscosity and C is the polymer concentration in the solution (12). This gives the intrinsic viscosity [η] as the extrapolated value on the ordinate, and an interaction parameter *b* from the slope. This Huggins equation can be applied to a solvent(1)/polymer(2)/polymer(3) ternary solution. This equation can yield $[\eta]_m$, which can be changed by an expansion or contraction of the polymer random coil, depending on whether the interactions between unlike i–j polymer segments are attractive or not. Also, the equation evaluates the

Received and Accepted May 2005.

Address correspondence to Omar Melad, Department of Chemistry, Al-Azhar University-Gaza, P.O. Box 1277, Gaza, Palestine, . E-mail: omarmelad@yahoo.com

viscometric interaction parameter b_m, that characterizes the overall hydrodynamic and thermodynamic interactions between like chains of the two polymers, and can thus be used to determine polymer-polymer compatibility. From the b_m parameter a thermodynamic $b_{23}^{(1)}$ parameter, is obtained that depends on the molar mass of the two polymers, on the weight fraction of each component, and/or on the concentration of each polymer in the solution. Usually the estimation of the compatibility of the polymer blends can be obtained by means of the sign of $\Delta b = b_{23}^{(1)} - b_{23}$ where $b_{23}^{(1)}$ and b_{23} are the experimental and the theoretical viscometric interaction parameter values. Specifically, the two polymers should be compatible if $\Delta b > 0$ and incompatible if $\Delta b < 0$.

In previous work by one of the present authors (13), it was established that the $b_{23}^{(1)}$ parameter depends on the concentration and weight fraction for the same molecular weight (2), but for different molecular weights (3) varies (depending upon the range of polymer weight fraction studied). These different dependences described in the literature have lead to confusion in defining a clear criterion for the compatibility. Most relevant here is the 1982 report by Lecourties et al. (14) estimating polymer compatibility for the ternary system solvent(1)/polymer(2)/polymer(3) by determination of the intrinsic viscosity of polymer(3) in a solvent containing a dilute solution of polymer(2). A new viscometric interaction parameter $b_{23}^{(2)}$ was defined that is independent of the concentration of polymer(3). Finally, the criterion $\Delta[\eta_3]_2 = [\eta_3]_2 - [\eta_3]$ may also be used to predict polymer-polymer compatibilities (15).

The present investigation uses this method to characterize the ternary system benzene(1)/PS(2)/PDMS(3), and to compare some of the various approaches mentioned above.

Theoretical

The theoretical consideration starts from the derivation by Krigbaum and Wall (16) and Cragg-Bigelow (17). The specific viscosity $\eta_{sp,m}$ of a mixed polymer solution can be expressed by

$$\begin{gathered} \eta_{sp,m} = \eta_{r,m} - 1 = \frac{t_{c2,c3}}{t_o} - 1, \text{ or:} \\ \eta_{sp,m} = [\eta_2]C_2 + [\eta_3]C_3 + b_{22}C_2^2 + b_{33}C_3^2 + 2b_{23}^{(1)}C_2C_3 \end{gathered} \tag{1}$$

where $[\eta_2]$ is the intrinsic viscosities of polymer 2 in the solution with the common solvent, C_2 is the concentration of polymer 2 in the mixed polymer solution, and $b_{23}^{(1)}$ is the interaction parameter for polymers 2 and 3.

For the system consisting of polymer(3) in a binary solvent (polymer(2) + solvent) at concentration C_2, Eq. (1) can be written as:

$$\begin{aligned} [\eta]_{3,c_2} &= \lim_{C_3\to 0} \frac{\eta_{sp_3,C_2}}{C_3} \\ &= \lim_{C_3\to 0} \frac{\left(t_{c2,c3}/t_o - 1\right)}{C_3} \\ &= \lim_{C_3\to 0} \frac{[\eta_3] + b_{33}C_3 + 2b_{23}^{(1)}C_2}{1 + [\eta_2]C_2 + b_{22}C_2^2} \end{aligned} \tag{2}$$

If the system is independent of polymer(3) concentration, $\lim_{c_3 \to 0} b_{23}^{(1)} = b_{23}^{(2)}$, and:

$$[\eta]_{3,c_2} = \frac{[\eta]_3 + 2b_{23}^{(2)}C_2}{1 + [\eta]_2 C_2 + b_{22}C_2^2} \tag{3}$$

then:

$$\frac{[\eta]_{3,C_2}}{C_2}(1 + [\eta]_2 C_2 + b_{22}C_2^2) = 2b_{23}^{(2)} + \frac{[\eta]_3}{C_2} \tag{4}$$

The $b_{23}^{(2)}$ parameter can be obtained from the ordinate at $x = 0$ of a linear dependence of the first term of Eq. (4) against $[\eta]_3/C_2$ for several values of M_3. It depends only on M_2 and C_2, but is independent of M_3 and C_3.

Experimental

Materials

Samples of PS were purchased from Aldrich (USA) with average weight-average molecular weights M_w of 4000, 20,000, and 170,000 g/mol. Samples of PDMS were also purchased from Aldrich with average molecular weights of 18,000, 38,900, 90,200, and 170,300 g/mol. Benzene from Fisher Chemicals was used as solvent.

Viscosity Measurements

All measurements were performed at 30°C ± 0.1 using a Cannon-Fenske type capillary viscometer that was immersed in a constant temperature bath. The viscometer was calibrated with different solvents. The stock solutions of each binary or ternary system were made by dissolving the polymer samples in filtered benzene up to concentration ~0.1 g/ml. An amount of PDMS was added to a solution of PS at various concentrations of PS. The elution time of each solution was then determined as the average of several readings. Kinetic energy corrections were taken into account for the evaluation of $[\eta]$ and viscometric interaction parameter b, determined by extrapolation to infinite dilution (zero solute concentration) and from the slope of the linear plots, respectively. The uncertainty in the observed measurements was estimated to be less than 5% for all the systems.

Results and Discussion

The intrinsic viscosities as well as the viscometric interaction parameters for the different binary systems at 30°C are compiled in Table 1. It can be observed that the intrinsic viscosities for the 170,300 g/mol PDMS sample and for the and for the 170,000 g/mol PS sample are the highest (as expected), while values of the interaction parameter b for the two binary polymer systems are the lowest. These data are required for the practical use of Eq. (4). Fig.1 shows the plots of the first term of Eq. (4) vs. $[\eta]_3/C_2$ for the benzene(1)/PS(2)/PDMS(3) for the specific example where $C_2 = 20 \times 10^{-4}$ g/ml at $M_2 = 4000$ g/mol. The data for the other concentrations of polymer(2) and at different molar masses of polymer(2) are tabulated in Table 2. These data allow the use of Eq. (4) to obtain $b_{23}^{(2)}$. All the plots gave linear dependences from which the ordinate at $x = 0$ is $b_{23}^{(2)}$. Figure 2 shows the plots of $b_{23}^{(2)}$ versus the polymer(2) concentrations at different molar masses of polymer(3). It can be observed that the $b_{23}^{(2)}$ parameter

Table 1

Intrinsic viscosities $[\eta]_2$ and viscometric interaction parameter b_{22} for the binary solvent(1)/polymer(2) at 30°C at different polymer molar masses M

System	M (g/mol)	$[\eta]_2$ (ml/g)	b_{22} (ml^2/g^{-2})
Benzene/PDMS	18,000	38.73	−2716
	38,900	43.63	−3061
	90,200	90.68	−5149
	170,300	100.9	−7420
Benzene/PS	4,000	42.94	−4157
	20,000	45.78	−3407
	170,000	136.5	−5098

increases as the polymer(2) concentration increases, passing through a maximum at $C_2 = 20 \times 10^{-4}$ g/ml, and then decreases rapidly. Rather than paying attention to the sign of $b_{23}^{(2)}$, the focus is now on the need for a thermodynamic parameter to describe the compatibility of the polymer mixture based on differences between its experimental and theoretical values. The first thermodynamic parameter chosen was $\Delta b = b_{23}^{(2)} - b_{23}$, and Table 3 show the values obtained for different PDMS molar masses (independent of C_3 concentration) at several C_2 values studied. Figure 3 shows a sharp increase in Δb values at $C_2 = 20 \times 10^{-4}$ g/ml at constant M_2 molar masses and C_2 concentration. The values of Δb are positive indicating the compatibility of the two polymers in solution. The second thermodynamic parameter based on the difference between the experimental and the theoretical values of $[\eta]$ which is $\Delta[\eta_3]_2 = [\eta_3]_2 - [\eta_3]$ for the polymer-solvent method was used to predict the polymer-polymer compatibility [14].

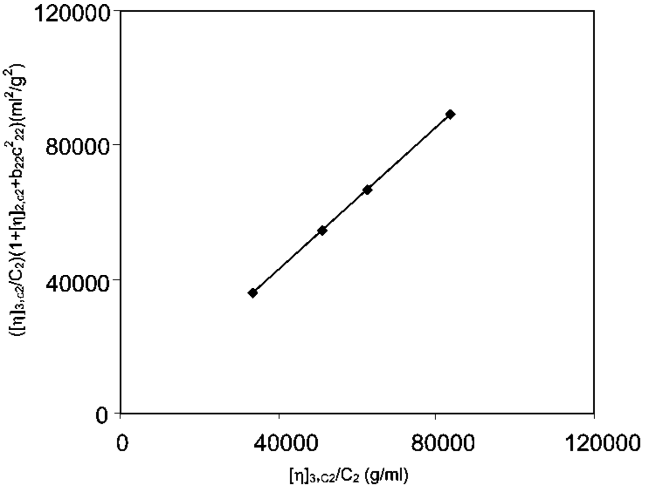

Figure 1. Plot of $([\eta]_{3,C_2}/C_2)\ (1 + [\eta]_{2,C_2} + b_{22}\, C_{22}^2)$ vs. $[\eta]_{3,C_2}$ for the system benzene(1)/PS(2)/PDMS(3), $C_2 = 20 \times 10^{-4}$ g/ml at $M_2 = 4000$.

Table 2

Intrinsic viscosity of polymer(3) in a binary solvent formed by solvent(1)/polymer(2), $[\eta]_{3,C_2}$, 30°C for different polymer(2) concentrations C_2, and for several molar masses of polymer(3) for the ternary system benzene(1)/PS(2)/PDMS(3)

M_3 (g/ml)	$10^4 \times C_2$ (g/ml)	$[\eta]_{3,C_2}$ (ml/g) $M_2 = 4000$	$[\eta]_{3,C_2}$ (ml/g) $M_2 = 20{,}000$	$[\eta]_{3,C_2}$ (ml/g) $M_2 = 170{,}000$
18,000	5	53.66	22.81	21.46
	10	46.40	26.83	13.42
	15	34.88	16.10	10.00
	20	81.83	78.10	29.50
	25	85.90	13.42	20.12
38,900	5	68.70	35.75	33.80
	10	59.17	47.00	26.10
	15	49.70	33.53	20.00
	20	102.2	88.75	48.80
	25	86.78	29.58	32.40
90,200	5	96.10	81.40	54.06
	10	78.09	80.30	60.07
	15	70.50	66.70	50.00
	20	124.8	100.0	78.60
	25	58.70	58.90	51.90
170,300	5	117.6	106.8	83.30
	10	94.91	114.6	102.7
	15	82.53	119.6	100.1
	20	127.93	138.7	128.1
	25	49.52	103.3	78.30

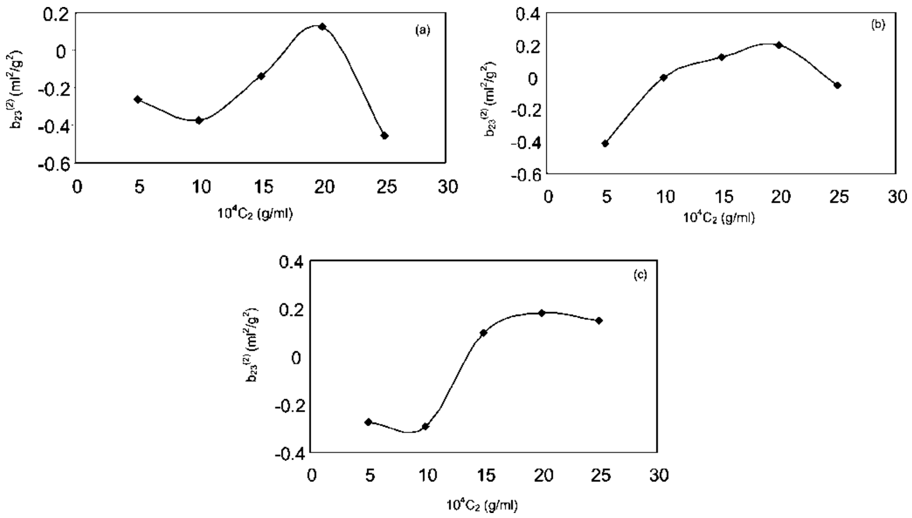

Figure 2. Plot of $b_{23}^{(2)}$ at a) $M_2 = 4000$ g/mol, b) $M_2 = 20{,}000$ g/mol and c) $M_2 = 170{,}000$ g/mol as a function of polymer(2) concentration, C_2 for the system benzene(1)/PS(2)/PDMS(3).

Table 3

Values of parameter $\Delta b = b_{23}^{(2)} - b_{23}$ for the ternary system benzene(1)/PS(2)/PDMS(3) at 30°C and at different molar masses of polymer(3)

$10^4 \times C_2$ (g/ml)	M_3 (g/ml)	Δb (ml^2/g^2) $M_2 = 4000$	Δb (ml^2/g^2) $M_2 = 20{,}000$	Δb (ml^2/g^2) $M_2 = 170{,}000$
5	18,000	3060.7	708.88	1185.0
	38,900	6193.7	1966.7	2147.7
	90,200	529.74	4147.7	1921.6
	170,300	4115.7	4516.7	3347.9
10	18,000	3177.6	1108.2	894.11
	38,900	5858.6	3165.1	1600.4
	90,200	4592.6	4209.1	2431.3
	170,300	1508.6	4969.1	4549.7
15	18,000	808.86	1148.3	691.60
	38,900	3814.8	1616.1	478.50
	90,200	3496.8	2804.1	1186.5
	170,300	2107.8	6015.1	5203.1
20	18,000	6812.1	5844.1	1689.2
	38,900	7513.1	6829.1	3165.6
	90,200	6742.1	7483.5	4206.1
	170,300	6467.1	6422.5	5344.1
25	18,000	3673.5	943.65	979.29
	38,900	4482.5	1357.1	3116.1
	90,200	2427.5	2915.9	2521.4
	170,300	3731.5	4755.9	2879.1

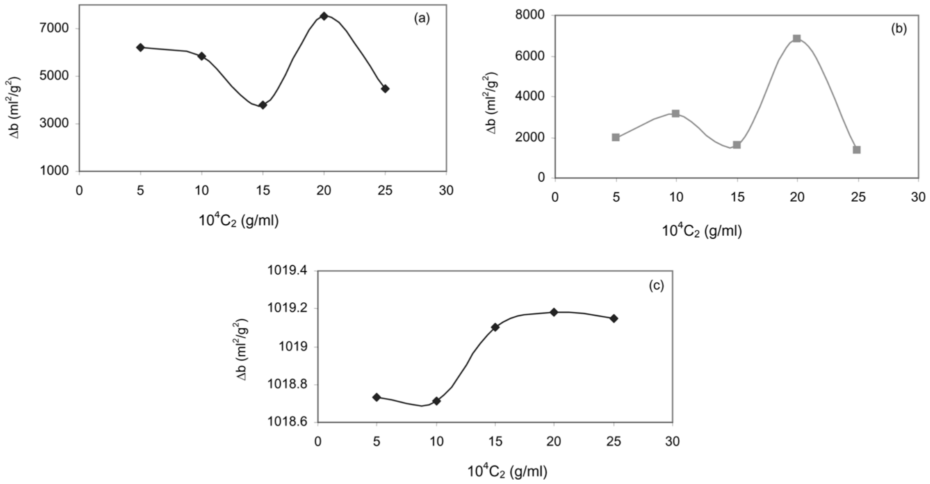

Figure 3. Plot of Δb at PDMS molar mass, 38 000 g/mol when a) $M_2 = 4000$ g/mol, b) $M_2 = 20{,}000$ g/mol and c) $M_2 = 107000$ g/mol as a function of polymer(2) concentration, C_2 for the system benzene(1)/PS(2)/PDMS(3).

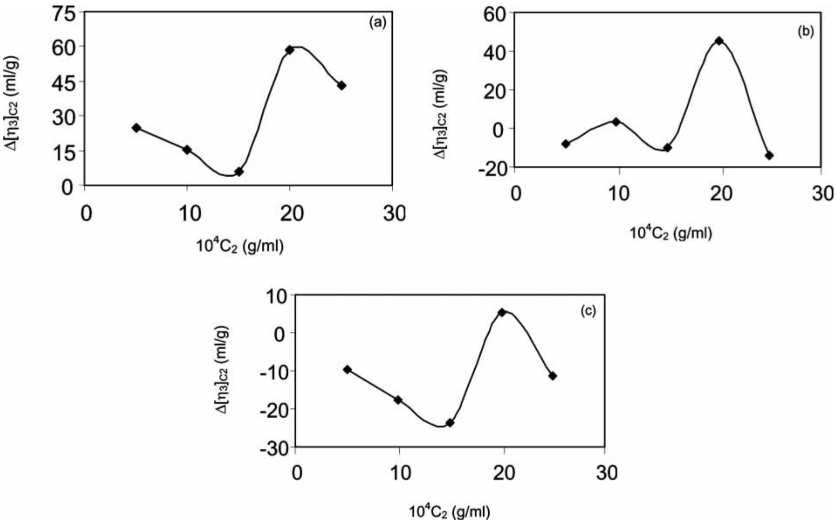

Figure 4. Plot of $\Delta[\eta_3]_{c2}$ at PDMS molar mass, 38,000 g/mol when a) $M_2 = 4000$ g/mol, b) $M_2 = 20{,}000$ g/mol and c) $M_2 = 107{,}000$ g/mol as a function of polymer(2) concentration, C_2 for the system benzene(1)/PS(2)/PDMS(3).

Table 4

Values of parameter $\Delta\,[\eta_3]_{c2} = [\eta_2]_{c2} - [\eta_3]$ for the ternary system benzene(1)/PS(2)/PDMS(3) at 30°C and at different molar masses of polymer(3)

$10^4 \times C_2$ (g/ml)	M_3 (g/ml)	$\Delta\,[\eta_3]_{c2}$ (ml/g) $M_2 = 4000$	$\Delta\,[\eta_3]_{c2}$ (ml/g) $M_2 = 20{,}000$	$\Delta[\eta_3]_{c2}$ (ml/g) $M_2 = 170{,}000$
5	18,000	14.93	−15.92	−17.27
	38,900	25.07	−7.88	−9.83
	90,200	5.42	−9.28	−36.62
	170,300	16.67	5.87	−17.63
10	18,000	7.67	−15.92	−17.27
	38,900	15.54	−7.88	−9.83
	90,200	−12.59	−10.38	−30.61
	170,300	−6.02	13.67	1.77
15	18,000	−3.85	−22.63	−28.73
	38,900	6.07	−10.10	−23.63
	90,200	−20.18	−23.98	−40.68
	170,300	−18.40	18.67	−0.83
20	18,000	43.10	39.37	−9.23
	38,900	58.57	45.12	5.17
	90,200	34.12	9.32	−12.08
	170,300	27.00	37.77	27.18
25	18,000	47.17	−25.31	−18.61
	38,900	43.15	−14.05	−11.23
	90,200	−31.98	−31.78	−38.78
	170,300	−51.41	2.77	−22.63

Specifically, if $\Delta[\eta_3]_2 \geq 0$, then polymer 2 and 3 are compatible whereas $\Delta\ [\eta_3]_2 \leq 0$ indicates that polymer 2 and 3 are incompatible. Figure 4 shows the variations of $\Delta[\eta_3]_2$ vs. C_2 when the values of M_3 are 38,900 g/mol and 170,300 g/mol as examples. The values ranged from negative to positive when $C_2 = 20 \times 10^{-4}$ g/ml, indicating good compatibility between the two polymers at that polymer(2) concentration. This is in agreement with the results from the first thermodynamic parameter Δb.

The present investigation has thus successfully provided useful insights into the compatibility of PS-PDMS mixtures, and this should encourage similar studies of other polymer-polymer mixtures.

Conclusions

The present study involved dissolving polymer(3) (guest polymer) into solution containing the second polymer (host polymer) at different C_2 concentration and M_2 molar mass and constant C_3. The compatibility of the two polymers was evaluated through experimental measurements of specific viscosities of polymer(3). Our previous relevant work focused on the interaction parameter $b_{23}^{(1)}$, which has disadvantageous multiple dependences. For the present PS-PDMS system, emphasis was therefore switched to another parameter $b_{23}^{(2)}$ independent of polymer(3) molar mass and concentration for all C_2. Values of $\Delta b = b_{23}^{(2)} - b_{23}$ indicate that for the system solvent(1)/polymer(2)/polymer(3), polymer(2) and polymer(3) are compatible either as the molar masses of polymer(3) increases for a given C_2 and M_2, or as C_2 increases for a given M_2. Finally, the results appear to have an advantageous independence of the M_3 concentrations.

Acknowledgments

It is a pleasure to acknowledge the financial support provided OM by the Fulbright Foundation, and the support provided JEM by the National Science Foundation through Grant DMR-0314760 (Polymer Program, Division of Materials Research).

References

1. Olabisi, O., Robeson, L.M., and Shaw, T. (1979) *Polymer-Polymer Miscibility*; Academic Press: New York.
2. Kulshreshtha, A.K., Singh, B.P., and Sharma, Y.N. (1988) Viscometric Determination of Compatibility in PVC/ABS Polyblends. Part III. Choice of a Common Solvent and its Effect on Results. *Eur. Polym. J.*, 24: 191–194.
3. Mamza, P.A.A.P. and Folaranmi, F.M. (1996) Compatibility Studies on Solution of Polystyrene and Polyvinyl Acetate Blend by Density and Viscometric Methods. *Eur. Polym. J.*, 32: 909–912.
4. Sun, Z.H., Wang, W., and Feng, Z.L. (1992) Criterion of Polymer-Polymer Miscibility Determined by Viscometry. *Eur. Polym. J.*, 28: 1259–1261.
5. Chee, K.K. (1990) Determination of Polymer-Polymer Miscibility by Viscometry. *Eur. Polym. J.*, 26: 423–426.
6. Kulshreshtha, A.K., Singh, B.P., and Sharma, Y.N. (1988) Viscometric Determination of Compatibility in PVC/ABS polyblends—I. Viscosity-Composition Plots. *Eur. Polym. J.*, 24: 29–31.
7. Kulshreshtha, A.K., Singh, B.P., and Sharma, Y.N. (1988) Viscometric Determination of Compatibility in PVC/ABS Polyblends—II. Reduced Viscosity-Concentration Plots. *Eur. Polym. J.*, 24: 33–35.

8. Montelro, E.E.C. and Thaumalurgo, C. (1993) Miscibility of PVA/EVA Systems by Viscometry. *Polym. Bull.*, 30: 697–703.
9. Lizymol, P.P. and Thomas, S. (1994) Binary Polymer Systems—Interactions in Solutions and Their Relationship to Solid State Compatibility. *Eur. Polym. J.*, 30: 1135–1142.
10. Danait, A. and Deshparrde, D.D. (1995) A Novel Method for Determination of Polymer-Polymer Miscibility by Viscometry. *Eur. Polym. J.*, 31: 1221–1225.
11. Zhu, P.P. and Wang, P. (1997) A New Criterion of Polymer-Polymer Miscibility Detected by Viscometry. *Eur. Polym. J.*, 33: 411–413.
12. Huggins, M.L. (1942) The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration. *J. Am. Chem. Soc.*, 64: 2716–2718.
13. Garcia, R., Melad, O., Gomez, CM., Figueruelo, J.E., and Campos, A. (1999) Viscometric Study on the Compatibility of Polymer-Polymer Mixtures in Solution. *Eur. Polym. J.*, 35: 47–55.
14. Lecourtier, J., Lafuma, F., and Quivoron, C. (1982) Study of Polymer Compatibilization in Solution Through Polymer/Polymer Interactions: Ternary systems Poly(ethylene oxide)/styrene-methacrylic Acid Copolymers/Solvent. *Makromol. Chem.*, 183: 2021–2031.
15. Melad, O. (2003) Viscometric Investigations on the Intrinsic Viscosity of Polyvinylpyrrolidone Affected by Polymer-Polymer Interactions in Solution (electronic journal). *Polymer*, 28.
16. Krigbaum, W.R. and Wall, F.T. (1950) Viscosities of Binary Polymeric Mixtures. *J. Polym. Sci.*, 5: 505–514.
17. Cragg, L.H. and Bigelow, C.C. (1955) A Molecular Weight-Intrinsic Viscosity Study Several Diene Polymers. *J. Polym. Sci.*, 16: 87–96.