

Miscibility of Polystyrene with Poly(ethylene oxide) and Poly(ethylene glycol)

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ABSTRACT: The intrinsic viscosity of polystyrene–poly(ethylene oxide) (PS–PEO) and PS–poly(ethylene glycol) (PEG) blends have been measured in benzene as a function of blend composition for various molecular weights of PEO and PEG at 303.15 K. The compatibility of polymer pairs in solution were determined on the basis of the interaction parameter term, Δb , and the difference between the experimental and theoretical weight-average intrinsic viscosities of the two polymers, $\Delta[\eta]$. The theoretical weight-average intrinsic viscosities were calculated by interpolation of the individual intrinsic viscosities of the blend components. The compatibility data based on $[\eta]$ determined by a single specific viscosity measurement, as a quick method for the determination of the intrinsic viscosity, were compared with that obtained from $[\eta]$ determined via the Huggins equation. The effect of molecular weights of the blend components and the polymer structure on the extent of compatibility was studied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1471–1482, 1998

Key words: intrinsic viscosity; specific viscosity; single point measurement; polystyrene; poly(ethylene oxide); poly(ethylene glycol)

INTRODUCTION

Modern technology needs new types of polymer materials, the properties of which are fitted to the particular use and may be even tuned in a sensitive way. To combine properties of two known polymers, it is often possible to copolymerize their monomers and prepare copolymers that do not only combine the properties of the homopolymers but sometimes exhibit valuable new properties. However, preparation of some copolymers may be difficult or outright impossible. Blending has become the least expensive and the most versatile way of achieving materials with new desirable properties.¹ The manifestation of superior properties depends upon the miscibility of the blend components at the molecular level.

Different techniques have been used to evaluate the compatibility of polymer blends. These techniques have involved thermal and mechanical methods^{2,3}; nuclear magnetic resonance (NMR) studies⁴; scattering techniques, such as the light scattering technique and neutron scattering, which provide valuable information about the thermodynamic behavior of blends^{5,6}; calorimetric data for concentrated solutions in low-molecular-weight solvents^{7,8}; measurement of vapor sorption⁴; inverse gas chromatography^{9,10}; and viscometry.^{11–17}

Viscometry becomes an attractive method for studying the compatibility of polymers in solution^{11–17} due to its simplicity. The basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blends lies in the fact that the repulsive interaction of the molecules of different polymers in solution may cause shrinkage of the polymer coils. This leads to a lower value of the viscosity of the polymer blend

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than the value calculated from viscosities of both pure components. On the other hand, the attractive interaction increases the viscosity of the system.

In our previous article,¹⁸ the miscibility of the two hydrophilic polymers [poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG)] was investigated. The present work discusses in detail the compatibility in solutions of PS–PEO and PS–PEG blends in benzene at 303.15 K by the viscometric technique. The regions of miscibility of PS–PEO and PS–PEG blends in terms of the interspecific interaction coefficient Δb and the difference in the intrinsic viscosities of the polymer blends and the weight-average intrinsic viscosities $\Delta[\eta]$ is one of the main objectives of this article. A comparison between the compatibility based on the $[\eta]$ obtained from the Huggins equation and that obtained by single measurements of specific viscosity is another goal of the present investigation.

EXPERIMENTAL

Materials

Benzene was dried over anhydrous MgSO_4 and filtered to be dried additionally over sodium wire before it was distilled at atmospheric pressure. The polystyrene (PS) sample of nominal polydispersity index $\bar{M}_w/\bar{M}_n = 1.06$ was obtained from Pressure Chemical Company, Pittsburgh, PA, USA. The quoted relative molar mass (M) was 110,000. Three PEO samples were obtained from Aldrich Chemical Co. Ltd. (UK). Their quoted relative molar masses were 1.0×10^5 , 3.0×10^5 , and 6.0×10^5 . These samples designated here as PEO1, PEO2, and PEO3, respectively. The nominal ratio of weight- to number-average molecular weights \bar{M}_w/\bar{M}_n for samples PEO1–PEO3 was less than 1.09. Three PEG samples were obtained from Aldrich Chemical Co. Ltd. (UK). The quoted relative molar masses for samples PEG1, PEG2, and PEG3, respectively, were 1.5×10^4 , 3.5×10^4 , and 1.0×10^5 .

Density and Viscosity

The density of pure benzene was measured at different temperatures dilatometrically, as described before.^{19,20} The dilatometer was calibrated with mercury to determine their volumes up to

a fixed mark and capillary radii. Details of the preparation of solutions, as well as measurements of $[\eta]$, have been described elsewhere.^{21–23} Viscosities of each polymer and polymer blend, covering the whole range of composition, were measured at 303.15 K in benzene by using dilution Ubbelohde viscometer having flow time of 80 s for pure benzene at 303.15 K. The viscosity data are quoted on the basis of the equations of Huggins²⁴ and Kraemer²⁵ [eqs. (1) and (2)], as follows:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c \quad (1)$$

$$\frac{\ln \eta_r}{c} = [\eta] - k_K[\eta]^2c \quad (2)$$

where η_{sp} , η_r , k_H , k_K are the specific viscosity, relative viscosity, Huggins viscosity slope constant, and Kraemer viscosity slope constant, respectively. The viscometer was calibrated with water, and the obtained data indicated that there was no need for applying end correction to the length of the capillary and kinetic energy correction for this particular viscometer.

RESULTS AND DISCUSSION

During the last two decades, viscometry methods have been successfully used to investigate and characterize compatibility of different pairs of polymers by Shih and Beatty,²⁶ Lizymol and Thomas,²⁷ and other research groups.^{28–30} Kulshreshtha et al.³¹ applied the viscosity method to the poly(vinyl chloride)–poly(acrylonitrile-*co*-butadiene-*co*-styrene) (PVC–ABS) blend system to study the compatibility. They found that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility.

Normally, the dilute solution viscometry is based on the classical Huggins equation²⁴ that expresses the specific viscosity (η_{sp}) of the polymer as a function of concentration c when one polymer is dissolved alone in the solvent [eq. (1)]. Krigbaum and Wall³² modified the Huggins equation and derived an expression of the viscosity $\eta_{(c_1, c_2)}$ of a dilute solution containing two polymers (1, 2) at concentrations (c_1 , c_2), as follows:

$$\frac{\eta_{(c_1, c_2)}}{\eta_0} - 1 = c_1[\eta_1] + c_2[\eta_2] + c_1^2b_1 + c_2^2b_2 + 2c_1c_2b_{12} + \dots \quad (3)$$

where $[\eta_i]$ is the intrinsic viscosity of polymer i in pure solvent, η_0 is the solvent viscosity, and b_{12} is the interaction coefficient between the two polymers.

The specific viscosity $\eta_{sp,m}$ of a mixed polymer solution can be expressed as follows if b_1 and b_2 are replaced by b_{11} and b_{22} and 5 terms only are considered:

$$\eta_{sp,m} = [\eta_1]c_1 + [\eta_2]c_2 + b_{11}c_1^2 + b_{22}c_2^2 + 2b_{12}c_1c_2 \quad (4)$$

For mathematical convenience, Krigbaum and Wall³² defined the interspecific interaction coefficient b_{12} as

$$b_{12} = \sqrt{b_{11}b_{22}} \quad (5)$$

The values of b_{11} and b_{22} are the slopes of the plots according to the Huggins equation for polymer (1) and polymer (2), respectively. The definition of b_{12} according to eq. (5) is not valid for systems that have negative values for b_{11} or b_{22} . Therefore, the modification by Williamson and Wright³³ is used to evaluate b_{12} , which can be expressed as

$$b_{12} = \frac{[b_{11} + b_{22}]}{2} \quad (6)$$

The value of b_{12} can be obtained from eq. (4) by determining the specific viscosity of the mixture, $\eta_{sp,m}$; the intrinsic viscosity of the pure components, $[\eta_i]$; and the value of b_{11} and b_{22} . Also, parameter b_{12} can be theoretically calculated from eq. (5) or eq. (6). The parameter b_{12} computed from any of these equations is defined as b_{12}^* . Krigbaum and Wall³² suggested that information about the interaction between two polymers should be obtained from the difference of experimental b_{12} and theoretical b_{12}^* . The difference was defined as Δb and expressed as

$$\Delta b = b_{12} - b_{12}^* \quad (7)$$

Equation (4) can be simplified to the form of eq. (8) at infinite dilution of the solution (that is, when c approaches zero).

$$\left[\frac{\eta_{sp,m}}{c} \right]_{c \rightarrow 0} = \sum_i [\eta_i] \frac{c_i}{c} = [[\eta]_1 w_1]_{c \rightarrow 0} + [[\eta]_2 w_2]_{c \rightarrow 0} \quad (8)$$

where w_1 and w_2 are the weight fractions of polymer (1) and polymer (2), respectively. This means that the intrinsic viscosity of a mixture of two polymers can be expressed as the weight-average viscosity of the intrinsic viscosities of the two polymers. For compatible systems, the observed intrinsic viscosities are reported to be higher than the calculated values.³³

Recently, the compatibility of solutions of PVC–poly(ethylene-*co*-vinyl acetate), PVC–poly(styrene-*co*-acrylonitrile), and poly(ethylene-*co*-vinyl acetate)–poly(styrene-*co*-acrylonitrile) has been characterized by a viscometry technique using the Krigbaum and Wall parameter, Δb , by Lizymol and Thomas.²⁷ Using the same technique, Chen et al.,³⁴ and Shih and Beatty,²⁶ respectively, determined the compatibility of PEO–poly(vinyl acetate) and polycarbonate–poly(hexamethylene sebacate) polymer pairs.

Hereafter, we shall discuss in detail the compatibility in solutions of PS–PEO and PS–PEG blends in benzene at 303.15 K by the viscometric technique. The calculation in the present work is based on the theoretical consideration by Krigbaum and Wall³² [eq. (4)], where the b_{12} parameter corresponds to the geometric mean of each polymer–solvent interaction parameter instead of the arithmetic mean of b_{12} [eq. (6)]. However, in some publications, eq. (6) is used because the definition of b_{12} according to eq. (5) is not valid for systems that have negative values for b_{11} or b_{22} . According to the approach of Krigbaum and Wall,³² comparison of experimental values of b_{12} with the theoretical values of b_{12} (b_{12}^*) could give information on interactions of the polymer pairs. A positive difference between the experimental and the theoretical viscosity interaction coefficients Δb refers to attractive interactions and is evidence of a compatible polymer pair. The higher the value of Δb , the higher the extent of compatibility. A negative value refers to repulsive interaction and incompatible mixes.

It is apparent that considerable time and effort would be saved if, instead of determining η_r for a series of solutions, a single determination at known concentration might be used to give $[\eta]$ directly. A number of equations^{35–45} have been suggested for quick determination of the $[\eta]$ from single-point measurement of specific viscosity at one concentration. The use of these equations has been derived under the supposition of constancy of k -values in eqs. (1) and (2) and the validity of the $k_H + k_K = 0.5$ relationship.

Several years ago, Solomon and Ciuta³⁵ derived their intrinsic viscosity relationship by combining eqs. (1) and (2). They arrived at eq. (9), as follows:

$$[\eta] = \frac{1}{c} \sqrt{2(\eta_{sp} - \ln \eta_r)} \quad (9)$$

These authors experimentally justified its validity on the grounds that $\frac{1}{c} \sqrt{2(\eta_{sp} - \ln \eta_r)}$ tends to $[\eta]$ as c tends to zero. The validity of this equation for measuring the $[\eta]$ via a single specific viscosity measurement was confirmed by the authors.¹⁸

In our previous article,¹⁸ we have derived a more precise equation for the determination of intrinsic viscosity from a single measurement of specific viscosity. This was done by the combination of Huggins and Schulz and Blaschke equations.⁴⁶ This was started by the rearrangement of the Huggins equation [eq. (1)] to the form of eq. (10), as follows:

$$\frac{\eta_{sp}}{[\eta]c} = 1 + k_H[\eta]c \quad (10)$$

Then, the value of $[\eta] = \frac{\eta_{sp}/c}{1 + k_{SB} \cdot \eta_{sp}}$ (the Schulz and Blaschke equation) was substituted in eq. (10) to obtain eq. (11), which leads to eq. (12), as follows:

$$\frac{\eta_{sp}}{[\eta]c} = 1 + k_H \frac{\eta_{sp}}{1 + k_{SB}\eta_{sp}} \quad (11)$$

$$[\eta] = \frac{\eta_{sp} + k_{SB}\eta_{sp}^2}{c + k_{SB}\eta_{sp}c + k_H\eta_{sp}c} \quad (12)$$

where k_{SB} is the Schulz–Blaschke viscosity slope constant.

It has been reported²⁴ that k_H in eq. (10) is constant for a large number of polymer solvent systems. While Khan et al.⁴⁷ reported a value of 0.28 for k_{SB} , our previous study afforded a value of 0.2648 ± 0.0033 for k_{SB} via a comprehensive statistical analysis of the measured values of k_{SB} for different polymer–benzene systems.

Equation (12) leads to the new method [eq. (13)] for measuring the $[\eta]$ via a single specific viscosity measurement, as follows:

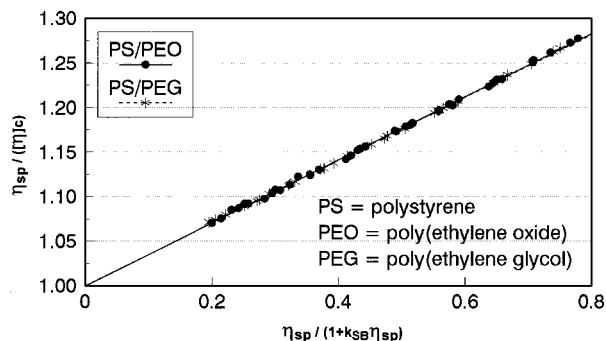


Figure 1 Plot according to eq. (11) to derive the Huggins viscosity slope constants for polystyrene–poly(ethylene oxide)–benzene and polystyrene–poly(ethylene glycol)–benzene systems.

$$[\eta] = \frac{\eta_{sp}(1 + 0.2648 \eta_{sp})}{c + \eta_{sp}(0.2648c + k_Hc)} \quad (13)$$

Since k_H should be constant for each polymer–solvent system, the plot of $\eta_{sp}/[\eta]c$ versus $\eta_{sp}/(1 + 0.2648 \eta_{sp})$, according to eq. (11), should give a straight line of slope k_H for each polymer–solvent system and a unique intercept equaling unity. This was tested by plotting the corresponding X–Y values for (PS–PEO)–benzene and (PS–PEG)–benzene systems, regardless of the molecular weight of the polymers, the composition of the blend, and the concentration of the polymer solution. The plot illustrated in Figure 1 indicates that all calculated values for each polymer blend–benzene system recline on the same straight line. Since the slopes of these lines are quite close (0.3542 for PS–PEO–benzene system and 0.3525 for PS–PEG–benzene system), these lines are difficult to be distinguished. The goodness of fits, as indicated by r^2 , were found to be higher than 0.999, and the intercepts, which are almost equal to unity reflect, the aptness of eq. (11). Accordingly, the values of 0.3542 and 0.3525 were used for estimating the intrinsic viscosity in benzene via eq. (13) for PS–PEO and PS–PEG blends.

The values of $[\eta]$ for pure polymers and their blends derived from Huggins and Kraemer plots by the aid of linear least-squares analysis, as well as $[\eta]$ from eq. (13) and k_H for pure polymers and polymer blends, are grouped in Table I. Values of b for pure polymers and b_{12}^* for different blends are also listed in the same table. Huggins and Kraemer plots are not presented here for brevity. It is of interest to mention that the recorded value of $[\eta]$ obtained from eq. (13) for each polymer or

Table I Intrinsic Viscosity, Interaction Coefficient (b), and Viscosity Slope Constant (k_H) at 303.15 K for Different Polymer–Benzene Systems

Polymer ^a (M wt $\times 10^{-5}$)	$[\eta]^b$ ($\text{dm}^3 \text{kg}^{-1}$)	$[\eta]^c$ ($\text{dm}^3 \text{kg}^{-1}$)	k_H	$b \times 10^{-4}$ [($\text{dm}^3 \text{kg}^{-1}$) ²]	
				b_{11} or b_{22}	b_{12}^*
PS 1.10	57.19	57.40	0.3551	0.1170	—
PEO1 1.00	98.04	98.30	0.3594	0.3473	—
PEO2 3.00	220.92	221.40	0.3608	1.7685	—
PEO3 6.00	362.38	363.00	0.3607	4.7525	—
PEG1 0.15	33.85	33.92	0.3623	0.0417	—
PEG2 0.35	52.98	53.10	0.3613	0.1019	—
PEG3 1.00	69.88	70.10	0.3596	0.1767	—
PS–PEO1 (25/75)	83.59	83.60	0.3536	—	—
PS–PEO1 (50/50)	74.64	74.70	0.3520	—	0.202
PS–PEO1 (75/25)	68.81	68.80	0.3549	—	—
PS–PEO2 (25/75)	162.05	162.10	0.3533	—	—
PS–PEO2 (50/50)	125.98	125.90	0.3562	—	0.455
PS–PEO2 (75/25)	90.03	90.10	0.3523	—	—
PS–PEO3 (25/75)	246.75	246.92	0.3533	—	—
PS–PEO3 (50/50)	181.12	181.08	0.3552	—	0.746
PS–PEO3 (75/25)	123.12	123.15	0.3542	—	—
PS–PEG1 (25/75)	37.42	37.45	0.3504	—	—
PS–PEG1 (50/50)	42.84	42.85	0.3524	—	0.069
PS–PEG1 (75/25)	47.05	47.00	0.3558	—	—
PS–PEG2 (25/75)	52.68	52.70	0.3536	—	—
PS–PEG2 (50/50)	53.23	53.25	0.3516	—	0.109
PS–PEG2 (75/25)	54.23	54.23	0.3529	—	—
PS–PEG3 (25/75)	76.39	76.32	0.3549	—	—
PS–PEG3 (50/50)	57.65	57.65	0.3526	—	0.144
PS–PEG3 (75/25)	55.40	55.38	0.3538	—	—

^a PS is polystyrene; PEO is poly(ethylene oxide); PEG is poly(ethylene glycol).

^b Obtained via eq. (13).

^c Obtained via the Huggins equation.

polymer blend is taken as an average for the $[\eta]$ values calculated from the specific viscosities of all concentrations. The specific viscosity data and Δb of all polymer blends having different compositions are tabulated in Tables II–IV.

Figure 2 shows the variation of Δb with the concentration of PS–PEO1 and PS–PEG3 blends as a function of the weight percent of both components and concentrations of the polymer blend at 303.15 K. It can be seen that the values of Δb are positive only for PS–PEO1 (75/25) and PS–PEG3 (25/75) blends; meanwhile, they are negative for other ratios. It is of interest to mention that the only compatible blends are achieved when the molecular weight of PEO and PEG are nearly equal to the molecular weight of PS (1.0

$\times 10^5$, 1.0×10^5 , and 1.1×10^5 , respectively, for PEO, PEG, and PS). This compatibility is detected only at a low percentage of PEO (25%) and at a high percentage of PEG (75%) of the total amount of the polymer mixture. This finding may be attributed to the similarity of the molecular weights of both components of the polymer mixtures. It may be assumed that PEO1 is dissolved in PS at a low percentage of PEO1; meanwhile, PS is dissolved in PEG at a low percentage of PS. On the other hand, Figures 3 and 4 show that all other PS–PEO and PS–PEG blends are incompatible, and the incompatibility increases, in general, with an increase in the content of PEO in the blend (Fig. 3), while it decreases with an increase in the PEG content in the blend (Fig. 4).

Table II Viscosity Data and Interaction Coefficient b_{12} and Δb at 303.15 K for Different Concentrations and Compositions of PS-PEO1 and PS-PEG3

PS-to-PEO Ratio	PS-PEO1				PS-PEG3			
	Conc. ($\times 10^3$)	η_{SP}	$-b_{12}$ ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)	Conc. ($\times 10^3$)	η_{SP}	$-b_{12}$ ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)
75 : 25	10.09	0.8691	0.256	-0.054	13.35	0.9365	0.014	0.158
	8.41	0.6996	0.260	-0.058	11.44	0.7779	0.032	0.176
	7.21	0.5847	0.265	-0.063	10.01	0.6646	0.050	0.194
	6.31	0.5019	0.270	-0.068	8.01	0.5139	0.086	0.230
	5.05	0.3908	0.282	-0.080	6.68	0.4186	0.122	0.266
	4.21	0.3197	0.293	-0.091	5.72	0.3528	0.154	0.298
	3.60	0.2704	0.321	-0.119	4.45	0.2684	0.221	0.365
					3.48	0.2064	0.302	0.446
50 : 50	10.11	0.9612	-0.109	0.093	12.02	0.8663	0.008	0.152
	8.67	0.7979	-0.095	0.107	10.52	0.7387	0.024	0.168
	7.58	0.6815	-0.086	0.116	9.35	0.6433	0.039	0.183
	6.74	0.5943	-0.074	0.128	8.42	0.5695	0.055	0.199
	5.52	0.4726	-0.049	0.153	7.01	0.4629	0.082	0.226
	4.67	0.3921	-0.029	0.173	6.01	0.3896	0.111	0.255
	4.05	0.3349	-0.007	0.195	4.68	0.2957	0.171	0.315
	3.19	0.2590	0.023	0.225	3.66	0.2271	0.239	0.383
	2.64	0.2111	0.072	0.274				
25 : 75	8.66	0.9134	0.005	0.207	9.54	0.9194	-0.539	-0.395
	7.58	0.7781	0.028	0.230	8.58	0.8099	-0.569	-0.425
	6.73	0.6771	0.044	0.246	7.15	0.6531	-0.626	-0.482
	6.06	0.5990	0.067	0.269	6.13	0.5465	-0.682	-0.538
	5.05	0.4863	0.106	0.308	4.77	0.4116	-0.798	-0.654
	4.33	0.4091	0.146	0.348	3.73	0.3141	-0.951	-0.807
	3.79	0.3528	0.188	0.390	2.86	0.2357	-1.159	-1.015
	3.03	0.2766	0.258	0.460				
	2.53	0.2275	0.346	0.548				

Note: PS is polystyrene; PEO1 is poly(ethylene oxide) (M wt 1.0×10^5); PEG3 is poly(ethylene glycol) (M wt 1.0×10^5).

Figures 2–4 reveal also that there are different influences of the total concentration of the mixture on Δb values. For incompatible blends, values of Δb increase with an increase in the concentration of the blend, while values of Δb decrease with the concentration of the mixture in case of miscible blends [PS-PEO1 (75/25) and PS-PEG3 (25/75)]. This may be attributed to the influence of the extent of the intermolecular and intramolecular interactions of the components of the ternary polymer solutions. At a very high solvent concentration, that is, at very high dilutions, the polymer-solvent interaction exceeds the polymer-polymer interaction. This phenomenon may be also explained by the shape and configuration of polymer molecules in the solution. In this respect, the polymer present in the lower concentra-

tion usually forms a discrete phase; whereas the polymer present in the higher concentration forms continuous phase, which enhances the polymer-polymer interaction. This leads to the speculation that Δb values of the above-studied polymer blends may approach zero or become positive values at very high concentrations, which, in turn, conveys to the assumption that these blends are compatible at solid state. The increase of the compatibility of PS with an increase in the percentage of PEG3 in the blend may be attributed to the increase of the number of functional groups (OH) in the blend. This increase in the functional groups forms a continuous phase of PEG instead of the discrete phase (domain) present at low content of OH groups. Under this condition, the PEG continuous phase acquires less intramolecular co-

Table III Viscosity Data and Interaction Coefficient b_{12} and Δb at 303.15 K for Different Concentrations and Compositions of PS-PEO2 and PS-PEO3

PS-to-PEO Ratio	PS-PEO2				PS-PEO3			
	Conc. ($\times 10^3$)	η_{SP}	$-b_{12}$ ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)	Conc. ($\times 10^3$)	η_{SP}	$-b_{12}$ ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)
75 : 25	7.53	0.8447	-0.018	0.437	5.61	0.8627	0.018	0.764
	6.70	0.7342	0.025	0.480	5.05	0.7605	0.081	0.827
	6.03	0.6488	0.064	0.519	4.59	0.6797	0.138	0.884
	5.48	0.5809	0.100	0.555	3.88	0.5601	0.242	0.988
	4.64	0.4801	0.179	0.634	3.36	0.4759	0.346	1.092
	4.02	0.4090	0.249	0.704	2.66	0.3656	0.602	1.348
	3.17	0.3152	0.383	0.838	2.10	0.2832	0.833	1.579
	2.62	0.2562	0.533	0.988	1.74	0.2310	1.127	1.873
50 : 50	6.09	0.9795	0.239	0.694	3.85	0.8716	1.594	2.340
	5.53	0.8724	0.279	0.734	3.57	0.7975	1.696	2.442
	5.07	0.7859	0.327	0.782	3.12	0.6810	1.917	2.663
	4.35	0.6554	0.425	0.880	2.78	0.5939	2.188	2.934
	3.80	0.5616	0.501	0.956	2.27	0.4723	2.623	3.369
	3.38	0.4910	0.596	1.051	1.85	0.3758	3.257	4.003
	2.77	0.3921	0.787	1.242	1.35	0.2664	4.341	5.087
	2.34	0.3263	0.939	1.394				
	1.96	0.2695	1.137	1.592				
25 : 75	4.60	0.9472	1.193	1.648	2.82	0.8705	5.059	5.805
	4.22	0.8525	1.306	1.761	2.54	0.7674	5.518	6.264
	3.62	0.7097	1.519	1.974	2.31	0.6858	5.961	6.707
	3.16	0.6073	1.678	2.133	1.95	0.5649	6.725	7.471
	2.81	0.5305	1.876	2.331	1.64	0.4625	7.894	8.640
	2.53	0.4706	2.081	2.536	1.33	0.3686	9.044	9.790
	2.11	0.3839	2.477	2.932	1.13	0.3062	10.836	11.582
	1.75	0.3118	3.012	3.467	0.92	0.2465	12.558	13.304
	1.49	0.2624	3.441	3.896				
	1.15	0.1992	4.338	4.793				

Note: PS is polystyrene; PEO2 is poly(ethylene oxide) (M wt 3.0×10^5); PEO3 is poly(ethylene oxide) (M wt 6.0×10^5).

hesive forces, and hence the specific interactions between the OH groups and the π -bonds of the phenyl rings of PS induce polymer miscibility.

The effect of molecular weight of PEO and PEG on their compatibility with PS can be detected from Figures 2–4 and from the data listed in Tables II–IV. For instance, values ranging from -0.274 to -0.093 , -0.694 to -1.592 , and -2.34 to -5.805 for Δb are assigned for (50/50 wt %) PS-PEO1, PS-PEO2 and PS-PEO3, respectively. On the other hand, values ranging from -0.138 to -0.051 , -0.12 to -0.047 , and -0.383 to -0.152 for Δb are assigned for (50/50 wt %) PS-PEG1, PS-PEG2, and PS-PEG3, respectively. This reveals that as the molecular weight of PEO increases from 1.0×10^5 to 6.0×10^5 , the negative value of Δb increases, which indicates

the increase of incompatibility of PEO with PS as the molecular weight of PEO increases. This behavior is shown more obviously in Figure 5, at which the variation of Δb with the concentration of different PS-PEO (75/25) blends is demonstrated. This finding indicates that the compatibility of PEO and PS is strongly dependent upon the molecular weight of PEO. This trend is not perfectly obeyed in PS-PEG system, in which PEG2 shows less incompatibility with PS in the ratios of 50/50 and 75/25. The deviation is pronounced for the PS-PEG (25/75) blends, as demonstrated in Figure 6, where the trend is just the opposite of PS-PEO blends. In this case, the incompatibility of PS-PEG (25/75) blends increases with the decreasing molecular weight of PEG. It is of interest to point out that the increase

Table IV Viscosity Data and Interaction Coefficient b_{12} and Δb at 303.15 K for Different Concentrations and Compositions of PS-PEG1 and PS-PEG2

PS-to-PEG Ratio	PS-PEG1				PS-PEG2			
	Conc. ($\times 10^3$)	η_{SP}	b_{12} ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)	Conc. ($\times 10^3$)	η_{SP}	b_{12} ($\times 10^{-4}$)	$-\Delta b$ ($\times 10^{-4}$)
75 : 25	16.01	0.9581	0.044	0.113	11.99	0.8021	0.043	0.066
	14.23	0.8309	0.054	0.123	9.99	0.6469	0.033	0.076
	12.81	0.7329	0.064	0.133	8.57	0.5415	0.021	0.088
	11.65	0.6554	0.074	0.143	7.49	0.4654	0.014	0.095
	9.85	0.5404	0.092	0.161	5.99	0.3629	-0.003	0.112
	8.54	0.4595	0.111	0.180	4.99	0.2973	-0.019	0.128
	6.74	0.3532	0.148	0.217	3.75	0.2182	-0.060	0.169
	5.57	0.2867	0.185	0.254				
	4.58	0.2319	0.235	0.304				
50 : 50	16.19	0.8665	-0.018	0.051	12.09	0.7931	0.062	0.047
	13.49	0.6975	-0.010	0.059	10.08	0.6399	0.054	0.055
	11.57	0.5829	-0.002	0.067	8.65	0.5360	0.046	0.063
	8.99	0.4382	0.011	0.080	7.56	0.4604	0.040	0.069
	7.36	0.3508	0.025	0.094	6.05	0.3591	0.026	0.083
	6.23	0.2923	0.039	0.108	5.04	0.2942	0.014	0.095
	4.49	0.2061	0.069	0.138	3.78	0.2159	-0.011	0.120
25 : 75	16.15	0.7356	-0.013	0.056	12.33	0.8010	0.061	0.048
	13.46	0.5945	-0.005	0.064	10.27	0.6461	0.054	0.055
	11.54	0.4984	0.004	0.073	8.81	0.5409	0.046	0.063
	8.97	0.3761	0.018	0.087	7.70	0.4648	0.042	0.067
	7.34	0.3019	0.033	0.102	6.16	0.3625	0.030	0.079
	5.05	0.2019	0.072	0.141	5.14	0.2969	0.014	0.095
					3.85	0.2179	-0.005	0.114

Note: PS is polystyrene; PEG1 is poly(ethylene glycol) (M wt 1.5×10^4); PEG2 is poly(ethylene glycol) (M wt 3.5×10^4).

in molecular weight of PEO and the decrease in molecular weight of PEG lead to molecular weights equable with the molecular weight of PS. Accordingly, Figures 5 and 6 confirm that the compatibility is attained only when the molecular weights of the two polymers become equable.

The derived values of $[\eta]$ obtained by the linear least-squares analysis and $\Delta[\eta]$ for polymer blends having different compositions measured are tabulated in Table V. The values of $\Delta[\eta]$ are used here as an alternative mean for determining the compatibility of polymer blends. In this respect, the viscosity of binary polymer solution (a single polymer dissolved in a solvent) expressed by the Huggins equation [eq. (1)] can be extended to a ternary polymer system (solvent-polymer 1-polymer 2) following the method proposed by Krigbaum and Wall³² and discussed in detail by Cragg and Bigelow.⁴⁸

$$\begin{aligned} \left(\frac{\eta_{sp}}{c} \right)_m &= [\eta]_m + b_m c \\ &= \sum_i [\eta]_i \frac{c_i}{c} + \left(\frac{\sum_i b_{ii}^{1/2} c_i}{c^{1/2}} \right)^2 \end{aligned} \quad (14)$$

where the subscript m refers to the ternary system, i is equal to 1 and 2 to each of the polymer components, and c equals $c_1 + c_2$ is the total concentration of the polymer blend. The parameter b_m summarizes the global interactions between all the segments in a polymer chain; no interactions between unlike i - j segments are included.

In eq. (14), the intrinsic viscosity of the mixture of polymers in a common solvent for a noninteracting system is expressed by eq. (8).

Most viscometric studies of polymer-polymer compatibility are based on the deviation of the

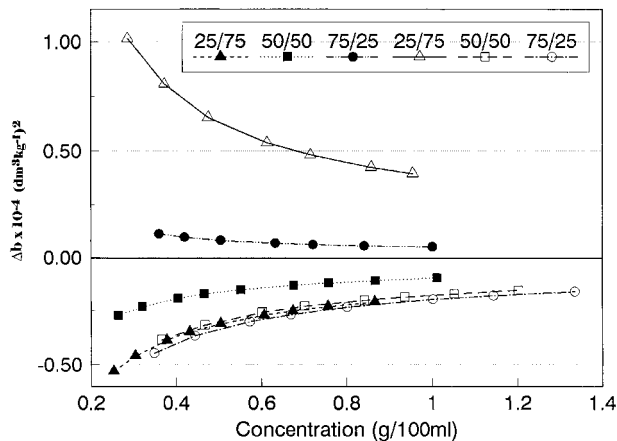


Figure 2 Variation of Δb with concentration for different ratios of PS-PEO1 (solid symbols) and PS-PEG3 (open symbols) at 303.15 K.

experimental $[\eta]_m^E$ from the theoretical $[\eta]_m^T$ values. In the present context, $\Delta[\eta]$ corresponds to the difference between $[\eta]_m^E$ and $[\eta]_m^T$. Hence,

$$\Delta[\eta] = [\eta]_m^E - [\eta]_m^T \quad (15)$$

The sign and magnitude of $\Delta[\eta]$ refers to the compatibility and incompatibility of the polymer pairs. The ideal behavior is attained when the value of $\Delta[\eta]$ equals zero, that is, $[\eta]_m^E$ and $[\eta]_m^T$ are equal. Under this condition, no interaction between the unlike polymers is present. The positive value of $\Delta[\eta]$ reflects an increase of the effective hydrodynamic specific volume, which suggests expansion of the coil due to favorable polymer 1-

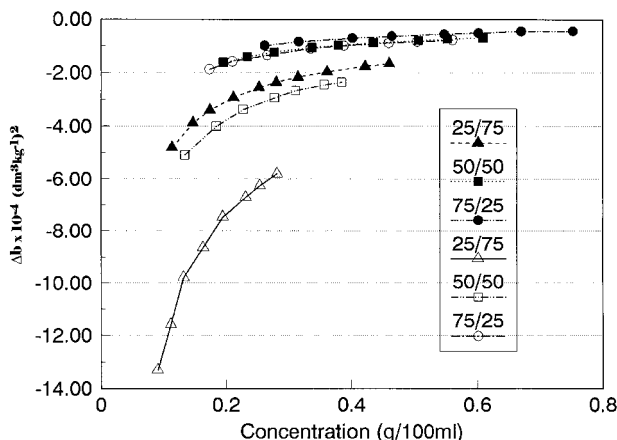


Figure 3 Variation of Δb with concentration for different ratios of PS-PEO2 (solid symbols) and PS-PEO3 (open symbols) at 303.15 K.

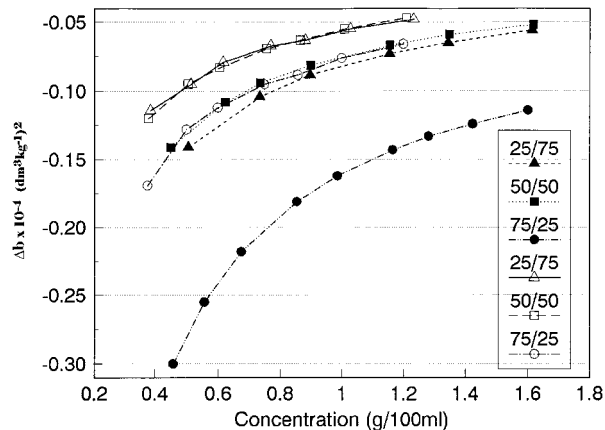


Figure 4 Variation of Δb with concentration for different ratios of PS-PEG1 (solid symbols) and PS-PEG2 (open symbols) at 303.15 K.

polymer 2 interaction. The negative value of $\Delta[\eta]$ means a repulsive interaction between the two polymers, and, hence, they are not likely to be compatible in the solid state. The experimental intrinsic viscosity, $[\eta]_m^E$, values for all polymer blends are tabulated in Table I, while the theoretical intrinsic viscosity, $[\eta]_m^T$, and $\Delta[\eta]$, calculated using eq. (15), are given in Table V. For the blends of PS-PEO1 and PS-PEG3, the data show positive deviations from ideal behavior, as manifested by the positive values of $\Delta[\eta]$ when the composition of the PS-PEO1 and PS-PEG3 blends are 75/25 and 25/75, respectively. All other compositions show negative deviation from ideal behavior and this deviation depends, to a large extent, on the molecular weight of PEO and

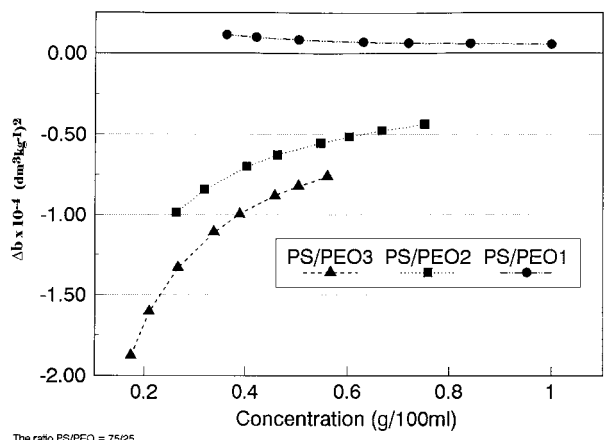


Figure 5 Variation of Δb with concentration for different mixtures of PS with PEO having different molecular weights at 303.15 K.

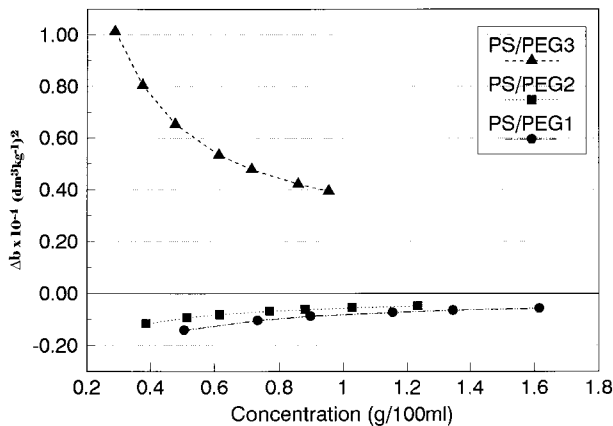


Figure 6 Variation of Δb with concentration for different mixtures of PS with PEG having different molecular weights at 303.15 K.

PEG. The Δb values of PS–PEO1 (75/25) and PS–PEG3 (25/75) compositions, as shown in Table II, are positive at all concentrations, indicating attractive interactions. This finding runs in har-

mony with the conclusion drawn by Lizymol and Thomas²⁷ and Walsh et al.⁴⁹ who stated that blends containing a higher proportion of functional group are more compatible.

With respect to the effect of molecular weight of PEO on its compatibility with PS, it can be seen from the data listed in Table V that the compatibility decreases with an increase in the molecular weight of the PEO. For instance, the values of $\Delta[\eta]$ for PS–PEO 50/50 blends are (–3.15), (–13.5), and (–29.12) for PEO1, PEO2, and PEO3, respectively. This increase in the negative deviation indicates that the compatibility of blends reduces with an increase in the molecular weight of PEO counterpart.

The $[\eta]$ values of the pure polymers and their blends, based on our new equation [eq. (13)] for determining the $[\eta]$ from a single specific viscosity measurement show values of $\Delta[\eta]$ in a good agreement with that obtained from the Huggins extrapolation method. This finding confirms the aptness of our equation in determining the intrinsic viscosity of polymers and polymer blends from a sin-

Table V Intrinsic Viscosity and $\Delta[\eta]$ at 303.15 K Derived from the Huggins Equation for Different PS–PEO–Benzene and PS–PEG–Benzene Systems

Polymer Blend	PS–PEO Ratio	$[\eta]_m^a$ ($\text{dm}^3 \text{kg}^{-1}$)	$-\Delta[\eta]^b$ $\text{dm}^3 \text{kg}^{-1}$	$[\eta]_m^c$ ($\text{dm}^3 \text{kg}^{-1}$)	$-\Delta[\eta]^c$ ($\text{dm}^3 \text{kg}^{-1}$)
PS–PEO1	75 : 25	67.40	–1.41	67.63	–1.18
	50 : 50	77.62	2.98	77.85	3.15
	25 : 75	87.83	4.238	88.08	4.48
PS–PEO2	75 : 25	98.12	8.09	98.40	8.30
	50 : 50	139.06	13.08	139.40	13.50
	25 : 75	179.99	17.05	180.40	18.30
PS–PEO3	75 : 25	133.49	10.37	133.80	10.65
	50 : 50	209.79	28.67	210.20	29.12
	25 : 75	286.08	39.33	286.60	39.68
PS–PEG1	75 : 25	51.36	4.31	51.53	4.53
	50 : 50	45.52	2.68	45.66	2.81
	25 : 75	39.69	2.27	39.79	2.34
PS–PEG2	75 : 25	56.14	1.91	56.33	2.10
	50 : 50	55.09	1.86	55.25	2.00
	25 : 75	54.03	1.35	54.18	1.48
PS–PEG3	75 : 25	60.36	5.32	60.58	5.20
	50 : 50	63.54	5.89	63.75	6.10
	25 : 75	66.71	–9.68	66.93	–9.40

^a PS is polystyrene; PEO is poly(ethylene oxide); PEG is poly(ethylene glycol). 1, 2, and 3 refer to the relative molar mass of the polymer sample, as indicated in Table I.

^b Obtained via eq. (13).

^c Obtained via the Huggins equation.

gle specific viscosity measurement. Accordingly, using eq. (13) for determining the miscibility of polymers saves time and effort.

Table V shows that the only mixtures that possess positive $\Delta[\eta]$ values are those that possess positive Δb . Accordingly, this leads to the conclusion that both types of analysis, $\Delta[\eta]$ and Δb , are completely consistent.

It has been reported²⁷ that compatibility studies by viscometry are in agreement with the solid-state miscibility analysis. Since the data of Δb reveal that the compatibility increases with an increase in the blend concentration in the solution, an assumption that these blends are compatible at solid state may be ascertained.

CONCLUSIONS

On the basis of positive differences between the experimental and the theoretical viscosity interaction coefficients, Δb , the compatibility of the blends was estimated. It was found that compatible blends were only achieved when the molecular weights of PEO and PEG were nearly equal to the molecular weight of PS. In this case, compatibility was detected for PS (75%)/PEO1 (25%) and PS (25%)/PEG3 (75%) blends.

In the systems investigated, the values of Δb for all immiscible blends increased with the total concentration of the blend. This was attributed to the increase in polymer-solvent interaction at higher concentrations of polymer solutions. This finding leads to the speculation that Δb values of the studied polymer blends may approach zero or become positive at very high concentrations. This leads to the assumption that these blends could be compatible when they are mixed and melted to be fabricated as solid articles. The derived values of $[\eta]$ obtained by the linear least-squares analysis of the Huggins extrapolation procedure and that obtained from eq. (13) were used as an alternative means for evaluating the compatibility of polymer blends based on $\Delta[\eta]$. The compatibility data that was obtained was found to be in good agreement with that obtained by Δb .

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