Available online at www.sciencedirect.com

SCIENCE DIRECT®

European Polymer Journal 42 (2006) 1105–1112

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Miscibility and interactions of polystyrene/polyolefine and polystyrene/poly(*n*-alkyl methacrylate) mixtures in dilute xylene solutions

Ante Jukić, Marko Rogošić, Zvonimir Janović *

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, P.O. Box 177, HR-10000 Zagreb, Croatia

Received 4 July 2005; received in revised form 4 October 2005; accepted 4 November 2005
Available online 20 December 2005

Abstract

The miscibility and intermolecular interactions between polystyrene (PS) and poly(ethylene-co-propylene) (EPC), as well as between PS and long-chain poly(alkyl methacrylates) (PAMA), namely, poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA), in dilute xylene solutions at 30 °C were studied. Investigated polymers are widely used as rheology modifiers, i.e. viscosity index improvers and pour point depressants for lubricating mineral oils. The specific and reduced viscosities of two- and three-component polymer solutions as well as intrinsic viscosities and Huggins' parameter values were determined as functions of the polymer mixture composition and overall polymer concentration. The reduced viscosity was found to be linearly dependent on the overall polymer concentration. The observed viscosities of polymer mixtures were intermediate to those of the mixture constituents; the values decrease in the order: EPC > PS > PAMA. The specific viscosities of all the polymer mixtures obtained as the experimental results and calculated applying the Catsiff–Hewett and Krigbaum–Wall theoretical equations were considered. Since all the polymer/polymer pairs showed the negative viscometric interaction parameter values ($\Delta b_{12} < 0$), the PS/EPC and EPC/PAMA mixtures were found to be immiscible. The observed repulsive molecular interactions originate from the differences in polymer composition and molar masses. This conclusion was supported by calculations employing the group contribution approach of Coleman, Graf and Painter. The calculated values of interaction parameters for (co)polymer blends, Λ_{12}, were 5.47, 6.42 and 13.1 J cm^{-3} for PS/PDDMA, PS/PODMA and PS/EPC, respectively.

Keywords: Polystyrene; Poly(ethylene-co-propylene); Poly(alkyl methacrylate); Polymer blends; Intermolecular interactions; Miscibility; Dilute solution viscometry

1. Introduction

It is well known that the addition of minor quantities of appropriate polymeric additives may significantly affect the rheological properties of liquids. A dissolved, flexible polymeric molecule will reach the conformation of an isolated statistical coil in dilute

---

* Corresponding author. Tel.: +385 1 4597 125; fax: +385 1 4597 142.
E-mail address: zjanov@fkit.hr (Z. Janović).

0014-3057/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2005.11.003

solution. The inherently large equilibrium dimensions of molecular coils will be determined by a number of superposed contributing effects, such as the effect of polymer structure, polymer/solvent interaction as well as polymer/polymer interaction. Most of these effects will vary depending on the temperature, polymer concentration and polymer molar mass. In addition, they will also be affected by the deformation rate in flowing systems [1]. Thus, by varying the type and content of a polymeric additive, its structure and its molar mass one may, in principle, control the dimensions of polymeric molecules in solvents and thus, influence the solution viscosity and its temperature dependence.

This feature finds its broad application in various fields, mostly connected to the flow properties of liquids. Polymeric additives are widely used as thickeners, crude oil flow improvers and drag reducers. One of the most important uses of polymeric additives is in the field of lubricating mineral oils [2,3]. The most efficient polymer classes for this purpose are ethylene/propylene amorphous copolymers (EPC), hydrogenated block and star styrene/butadiene and styrene/isoprene copolymers and poly(alkyl methacrylates) (PAMA). Mixtures of polymers belonging to different classes may exhibit complementary or synergistic effects on the rheological properties of liquids [4]. Thus, the addition of EPC component is expected to significantly increase both the viscosity and the shear stability of lubricating mineral oils; the PAMA component will particularly improve the temperature dependent properties, i.e. it will raise the viscosity index value and lower the pour point temperature [5–8].

In our previous papers some results concerning the kinetics of radical copolymerizations of long and short chain alkyl methacrylates and styrene have been published [9,10]. The prepared additives were tested as viscosity improvers in base mineral oil solutions [9]. However, when testing the mixed polymeric additives consisting of EPC and various PAMAs, an overall decrease of viscosity of base mineral oil as well as xylene (model solvent) solutions has been observed [8,11]. That indicated that there was a significant degree of immiscibility between polymeric molecules of different types, a feature that is quite common for polymer blends. It was easily explained within the framework of the Flory–Huggins theory, using the concepts of molecular repulsion and coil shrinkage, and quantified using the group contribution approach of Coleman et al. [12]. Nevertheless, the results [11] have shown that at least one additional phenomenon, i.e. the intermolecular association of PAMA molecules has to be taken into account.

A similar investigation is presented in this paper. The miscibility and intermolecular interactions were studied by the dilute solution viscometry method (described e.g. in [13–16]), in mixed additive systems consisting of PS and EPC, as well as in PS/long-chain alkyl methacrylate systems. The long-chain PAMA component was either poly(dodecyl methacrylate) (PDDMA) or poly(octadecyl methacrylate) (PODMA). The xylene solutions at 30 °C were investigated.

2. Theory

The application of dilute solution viscometry method for the study of interactions and miscibility phenomena in dilute multicomponent polymer solutions has been described in more details elsewhere [17]. The most important features will be given here.

The concentration dependence of viscosity of ideal ternary polymer solutions of the polymer 1 + polymer 2 + solvent type is usually described by equations like that of Krigbaum and Wall [18]:

$$\frac{\eta_{\mathrm{sp}}}{c_1+c_2} = [\eta]_1 w_1 + [\eta]_2 w_2 + (k_{\mathrm{H1}}[\eta]_1^2 w_1^2 + k_{\mathrm{H2}}[\eta]_2^2 w_2^2 + 2b_{12}^{*} w_1 w_2)(c_1+c_2) \tag{1}$$

or that of Catsiff and Hewett [19]:

$$\frac{\eta_{\mathrm{sp}}}{c_1+c_2} = [\eta]_1 w_1 + [\eta]_2 w_2 + (k_{\mathrm{H1}}[\eta]_1^2 w_1^2 + k_{\mathrm{H2}}[\eta]_2^2 w_2^2 + 2b_{12}^{**} w_1 w_2)(c_1+c_2). \tag{2}$$

Here η_{sp} denotes the specific viscosity, $[\eta]$ is the intrinsic viscosity (limiting viscosity number), c is the mass concentration of polymer and k_{H} is Huggins' constant, which may be related to the thermodynamic quality of solvent. The composition dependence of viscosity in ternary systems is described by relative mass fractions of dissolved polymers, w_i. Both of these equations reduce to empirical Huggins's equation for binary polymer solutions in absence of the second polymeric component ($c_2 = 0$):

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta] + k_{\mathrm{H}}[\eta]^2 c = [\eta] + bc. \tag{3}$$

In previous equation the slope of Huggins' equation, b, is defined. It serves for the description of ideal behavior of ternary polymer solutions; "ideal" quantities b_{12}^{*} and b_{12}^{**} are calculated by

$$b_{12}^{*} = \sqrt{b_1 \times b_2} \tag{4}$$

and

$$b_{12}^{**} = \frac{b_1 + b_2}{2}, \tag{5}$$

respectively.

In the infinite dilution limit, both Krigbaum–Wall's and Catsiff–Hewett's expression reduce to the miscibility rule of Philippoff [20]:

$$[\eta]_{12} = [\eta]_1 w_1 + [\eta]_2 w_2. \tag{6}$$

It is possible to replace the "ideal" terms b_{12}^{*} and b_{12}^{**} in Eqs. (1) and (2) by an empirically defined quantity, b_{12}. A purely empirical relation is then obtained that may be used to the fit the linear dependence of specific viscosity on total polymer concentration in the low-concentration range, observed in non-ideal ternary solutions. The obtained relation may be formally identified with Huggins' expression (3):

$$\frac{\eta_{\mathrm{sp}}}{c_1 + c_2} = [\eta] + k_{\mathrm{H}}[\eta]^2 (c_1 + c_2) = [\eta] + b_{\mathrm{M}}(c_1 + c_2). \tag{7}$$

The extent of the deviation of experimental from "ideal" b-values may be used to quantify the interactions between polymeric components of a system under consideration. The quantities of interest (miscibility criterion variables, relative form) are defined as [17]:

$$\Delta b_{\mathrm{rel}}^{*} = \frac{b_{12} - b_{12}^{*}}{b_{12}^{*}} \tag{8}$$

and

$$\Delta b_{\mathrm{rel}}^{**} = \frac{b_{12} - b_{12}^{**}}{b_{12}^{**}}, \tag{9}$$

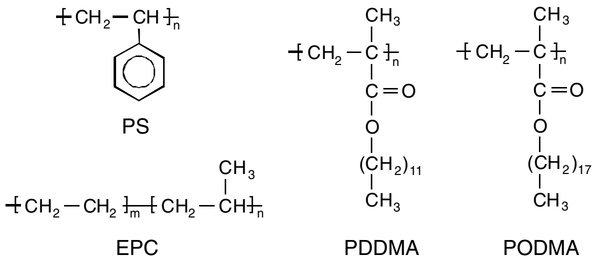
respectively. The negative values of miscibility criterion variables imply repulsive interactions (immiscibility of polymers); positive values imply attractive interactions (miscibility).

According to Eqs. (1) and (2), the b_{12}-value should be considered constant for a non-ideal ternary system, just like the b_{12}^{*} or b_{12}^{**}-values are in ideal systems. However, in previous article [11] we have shown that this need not be true in systems exhibiting self-association of at least one polymeric component. Systems involving PAMAs certainly belong to that class of systems [21–23].

3. Experimental

3.1. Materials

In this investigation, four different polymers were used. Poly(ethylene-co-propylene) (EPC) was a commercial product (Lubrizol 7067) of Lubrizol Chem. Co. The molar fraction of ethylene units was found to be 60%, as deduced by the ^{1}H NMR spectroscopy. Polystyrene (PS), poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA) were synthesized by the free radical polymerization of corresponding monomers in xylene solution at 90 °C, using *tert*-butyl peroxy-2-ethylhexanoate (Akzo Chemicals) as an initiator. The detailed procedure was described in the previous paper [10]. Xylene of high purity (Kemika, Zagreb, Croatia, p.a.) was used as received.



3.2. Methods

Binary polymer solutions were prepared by dissolving the appropriate mass of polymers in xylene, followed by dilution to a measured volume. Ternary polymer solutions were prepared by mixing the two corresponding binary solutions. Viscometric measurements were carried out at 30 ± 0.02 °C, using the Cannon–Fenske 50 K capillary viscometer immersed in a constant temperature bath. Relative viscosities of polymer solutions were calculated by dividing the flow times of solutions by that of the pure solvent ($\eta_{\mathrm{rel}} = \eta/\eta_0 = t/t_0$). The experiments were performed in the range of $1.05 < \eta_{\mathrm{rel}} < 1.5$ to provide typically five data points. The full range of polymer mixture compositions was investigated. No kinetic energy corrections were made due to the observed high value of solvent flow time. The reproducibility of experiments was ensured by measurement replication. For that purpose, ternary polymer solutions were made from newly prepared binary polymer solutions. No significant difference between replicated measurements was observed.

Table 1
Number, weight and z-average molar masses of EPC and synthesized polystyrene (PS), poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA)

	M_n (kg mol^{-1})	M_w (kg mol^{-1})	M_z (kg mol^{-1})
PS	108.5	213.4	379.6
EPC	59.1	108.9	166.7
PDDMA	34.2	73.0	135.1
PODMA	34.3	71.7	129.3

The ^{1}H NMR spectrum of EPC copolymer was recorded on the 90 MHz Varian EM-360 spectrometer at room temperature, in deuterated chloroform with TMS as an internal standard. The molar mass distributions of investigated polymers were determined by the size exclusion chromatography (SEC) carried out on the GPC-20 Polymer Laboratories instrument fitted with RI detector. Tetrahydrofuran was used as a solvent. Molar masses were calculated as polystyrene equivalents and their average values are listed in Table 1.

4. Results and discussion

A general discussion on the miscibility of investigated copolymer blends, either in solid state or in ternary polymer solutions, may start with some simple calculations, as described in our previous article [11]. A good starting point is the solubility parameter theory of Scatchard and Hildebrand. A modification of the theory is to be utilized when dealing with copolymers, such as EPC, to include the effect of internal repulsion of copolymer constituent units. Ten Brinke, Karasz and MacKnight have described the principle of internal repulsion that may promote mutual polymer/copolymer or copolymer/copolymer miscibility [24]. According to their approach, any unfavorable (repulsive) interaction between copolymer units covalently fixed within the same molecule may be relaxed by the addition of a secondary chemical species, in this case some other (co)polymeric component. Such a relaxation may be sensed only if a close contact between chemically different species is realized by mixing on molecular level. Thus the miscibility may be found even in the systems when none of the relevant homopolymer pairs exhibits favorable interactions. An equation is presented [25] that allows for the existence of negative values of interaction energy parameter, Λ_{12}, that are characteristic for miscible (co)polymer pairs:

$$\begin{aligned}\Lambda_{12} = {} & \Lambda_{\mathrm{AC}}\varphi_{\mathrm{A1}}\varphi_{\mathrm{C2}} + \Lambda_{\mathrm{AD}}\varphi_{\mathrm{A1}}\varphi_{\mathrm{D2}} \\ & + \Lambda_{\mathrm{BC}}\varphi_{\mathrm{B1}}\varphi_{\mathrm{C2}} + \Lambda_{\mathrm{BD}}\varphi_{\mathrm{B1}}\varphi_{\mathrm{D2}} \\ & - \Lambda_{\mathrm{AB}}\varphi_{\mathrm{A1}}\varphi_{\mathrm{B1}} - \Lambda_{\mathrm{CD}}\varphi_{\mathrm{C2}}\varphi_{\mathrm{D2}}. \end{aligned} \tag{10}$$

In this equation φ_{Kp} denotes the volume fraction of comonomer units K in copolymer p. Λ_{KJ} are the corresponding homopolymer interaction parameters that may be calculated by the well known Scatchard–Hildebrand term, i.e. the squared solubility parameter difference:

$$\Lambda_{\mathrm{JK}} = (\delta_{\mathrm{J}} - \delta_{\mathrm{K}})^2. \tag{11}$$

Relevant δ_{J} and δ_{K}-values may be found experimentally. However, one may utilize the group contribution concept by Coleman et al. [12] to calculate the so-called non-hydrogen-bonding interaction parameters. The necessary data are given in Table 2. To account for the possible internal repulsion within long-chain alkyl methacrylate molecules (PDDMA and PODMA), we considered them as random copolymers of the polar methacrylate backbone and the bulky alkyl side chains.

Using the described approximations, we calculated the Λ_{12}-values for investigated (co)polymer pairs. The data are presented in Table 3, together with corresponding ΔG_{M}-values of Gibbs' free energy of mixing. These were calculated for equal volume fractions of polymer components ($\phi_i = 0.5$) by using a form of the Flory–Huggins equation:

$$\Delta G_{\mathrm{M}} = RT\left(\frac{\phi_1}{v_1}\ln\phi_1 + \frac{\phi_2}{v_2}\ln\phi_2\right) + \Lambda_{12}\phi_1\phi_2, \tag{12}$$

where v_i stands for the molar volume of polymer component i, R is the universal gas constant and T is the absolute temperature.

The results clearly indicate that Λ_{12}-data are far above the upper limit of miscibility of $\Lambda_{12} \approx 0.05$ J cm^{-3}, declared for poorly interacting polymers. Therefore, the theory predicts that phase

Table 2
Group contribution parameters of the Coleman–Graf–Painter method [12] used for the calculation of polymer interaction parameters

Group	V_i^* (cm^3 mol^{-1})	F_i^* (J$^{0.5}$ cm$^{1.5}$ mol^{-1})	M_i (g mol^{-1})
$-CH_3$	31.8	446	15
$-CH_2-$	16.5	270	14
$>CH-$	1.9	47	13
$>C<$	−14.8	−198	12
$-OCO-$	19.6	610	44
$-C_6H_5$	75.5	1503	77

Table 3
Thermodynamic interaction parameters for polystyrene/poly(ethylene-co-propylene) and polystyrene/poly(dodecyl methacrylate) or poly(octadecyl methacrylate) mixtures as solid blends, based on the group contribution approach

	A_{12} (J cm^{-3})	ΔG_M (J cm^{-3})
PS/PDDMA	5.47	1.35
PS/PODMA	6.42	1.59
PS/EPC	13.1	3.26

separation is expected to occur in all the investigated polymer mixtures, at least in their solid blend form. As pointed out in our previous article [11], the internal repulsion effect is known to promote the miscibility in similar systems; the abandonment of the unrealistic copolymer approximation for PAMAs would make the calculated figures even higher, and the calculated phase separation even more pronounced.

The addition of a solvent makes the above described interaction pattern much more complicated. In the first instance, the solvent itself may act as a relaxing agent for unfavorable intramolecular interactions in copolymers, thus diminishing the effect of the second (co)polymeric component, and increasing the mutual solubility of polymers. The extent of the effect will depend on the balance of copolymer segment/solvent interactions. In the case of excessive amounts of added solvent, i.e. in the infinite dilution limit, there will be no effect of intermolecular interactions at all. In the dilute solution range, (co)polymer molecules are no longer entangled and behave like a set of more or less isolated statistical coils. The local concentration of polymer segments is therefore not equal to the overall concentration and this presents the violation of the mean field approximation, used in derivation of Eqs. (10) and (12).

At finite, but low, concentrations of polymer molecules, one may expect that the dimensions of (co)polymer coils will depend primarily on intramolecular interactions as well as on polymer/solvent interactions. However, the coils will sense the influence of homo- and hetero-intermolecular interactions, too. Homo-intermolecular interactions, including possible self-association, will affect different property–concentration relationships, among which the viscosity–concentration dependence will be probably the most important one. The effect of unfavorable, repulsive hetero-intermolecular interactions will tend to be diminished by reducing the number of contacts allowing for such an interaction. This will result in shrinkage of polymer coils with respect to their dimensions in binary polymer/solvent systems. Vice versa, the attractive, favorable hetero-intermolecular interactions characteristic for polymer/polymer miscibility will cause the enlargement of polymer coils. Since the viscosity of a dilute polymer solution depends primarily on dimensions of polymer coils [1,21], the dilute solution viscometry method may serve as a suitable tool for studying the hetero-intermolecular interactions in ternary systems of the (co)polymer 1/(co)polymer 2/solvent type [17]. Any repulsive interaction will result in diminished viscosity and, vice versa, any attractive hetero-intermolecular interaction will tend to increase the viscosity of a ternary polymer solution.

All of the ternary systems studied in this work were meant to be tested as viscosity improvers for lubricating mineral oils; some of them will hopefully find their final use in a dissolved form, and their key application property will be the solution viscosity. This again confirms the dilute solution viscometry as a method-of-choice for the presented investigation. The experimental and calculating framework lying behind the method seems to be rather simple; the basic equations are given in the theoretical section of the article.

Experimentally determined reduced viscosities ($\eta_{red} = \eta_{sp}/c = (\eta_{rel} - 1)/c$) are shown in Figs. 1–3 for the PS/EPC/xylene, PS/PDDMA/xylene and PS/PODMA/xylene systems, respectively, as functions of total polymer concentration, $c = c_1 + c_2$. Huggins' extrapolation lines (linear regression coefficients > 0.99) are indicated, as well. One may observe that all the investigated systems follow the linear concentration dependence proposed by Huggins.

In Figs. 4–6 limiting viscosity numbers, $[\eta]$, are plotted vs. relative mass fractions of PS component, for the PS/EPC/xylene, PS/PDDMA/xylene and PS/PODMA/xylene systems, respectively. One immediately observe departures of the $[\eta]$-values from the $[\eta]_{12}$-values predicted by the combining rule of Philippoff, Eq. (6). The departures are mainly positive, but somewhat lower in comparison to those found in our previous investigations [11] in similar systems (<5% in comparison to <12%). The explanation presented therein may be repeated here: the observed departures are probably the consequence of imperfections of the extrapolation procedure. A significant negative deviation of the slope of Huggins' line, as induced by the repulsive

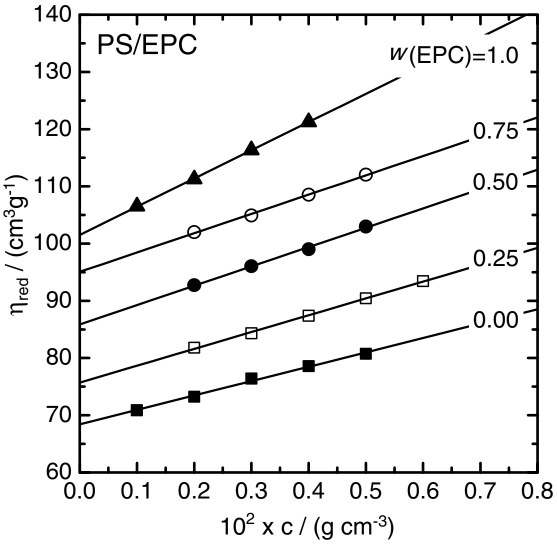


Fig. 1. Reduced viscosity dependence on total polymer concentration and composition of polystyrene and poly(ethylene-co-propylene) mixture, in xylene solution at 30 °C.

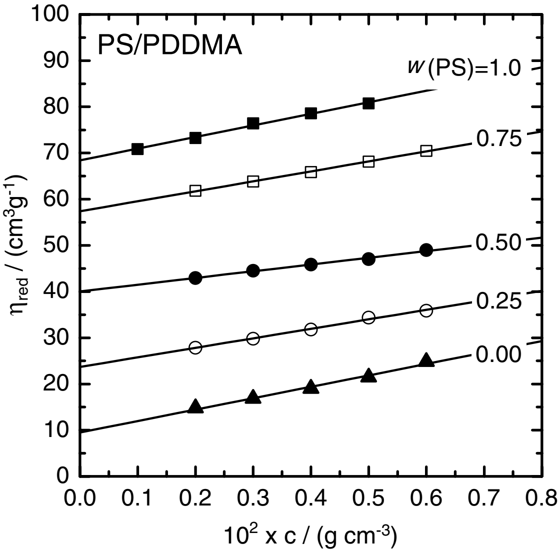


Fig. 2. Reduced viscosity dependence on total polymer concentration and composition of polystyrene and poly(dodecyl methacrylate) mixture, in xylene solution at 30 °C.

interactions between polymeric components, produces a slight, systematic and reproducible positive deviation of the intercept, [η].

Negative deviations of the slopes of Huggins' lines in ternary systems are normally interpreted as a consequence of immiscibility of (co)polymeric components. Such deviations come from the diminished viscosity of ternary polymer solutions, which is, in turn, caused by the shrinkage of polymer molecule coils, as discussed before. The results presented in Table 3 predict the immiscibility of all investigated polymer pairs; this accounts for at least a part of the Huggins' slope (and intercept) deviations. However, if excessive deviations are observed, one has to take into consideration other explanations, such as the effect of self-association of polymeric molecules.

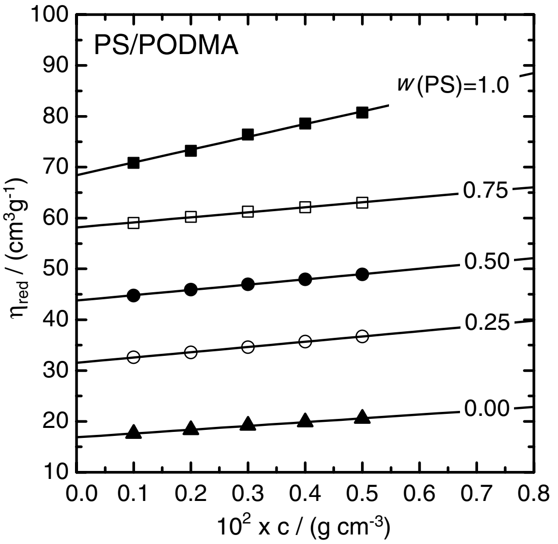


Fig. 3. Reduced viscosity dependence on total polymer concentration and composition of polystyrene and poly(octadecyl methacrylate) mixture, in xylene solution at 30 °C.

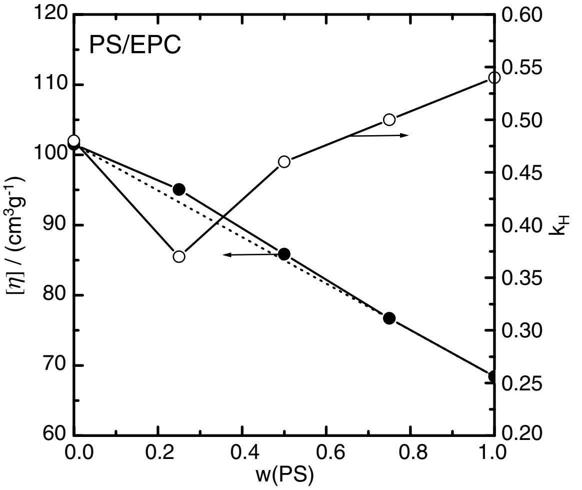


Fig. 4. Limiting viscosity number [η] and Huggins constant (k_H) dependence on relative mass fraction of polystyrene in mixture with poly(ethylene-co-propylene), in xylene solution at 30 °C. Dotted line indicates the miscibility rule of Philippoff.

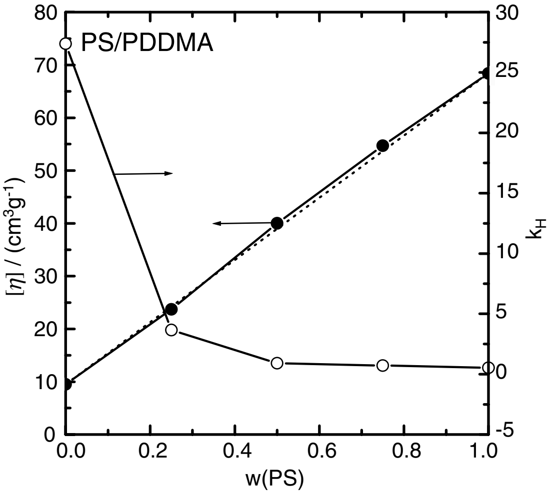


Fig. 5. Limiting viscosity number [η] and Huggins constant (k_H) dependence on relative mass fraction of polystyrene in mixture with poly(dodecyl methacrylate), in xylene solution at 30 °C. Dotted line indicates the miscibility rule of Philippoff.

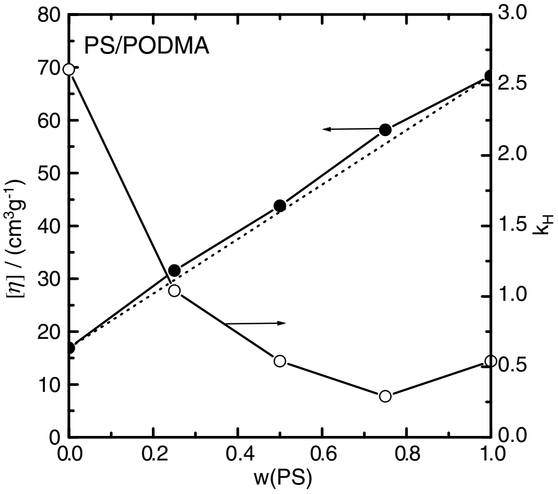


Fig. 6. Limiting viscosity number [η] and Huggins constant (k_H) dependence on relative mass fraction of polystyrene in mixture with poly(octadecyl methacrylate), in xylene solution at 30 °C. Dotted line indicates the miscibility rule of Philippoff.

In Figs. 4–6, k_H-values are plotted vs. relative mass fractions of PS component, for the PS/EPC/xylene, PS/PDDMA/xylene and PS/PODMA/xylene systems, respectively, besides the corresponding limiting viscosity numbers. The system without a PAMA component, i.e. the PS/EPC/xylene system exhibits moderate k_H-values for both homopolymers (0.48 and 0.54 for EPC and PS, respectively). The value for EPC corresponds with previously published value of 0.4 [11] that is characteristic for thermodynamically good solvent. The value for PS is somewhat higher, indicative for solvents of lower quality in the thermodynamical sense. The difference is, however, rather low in comparison to the experimental uncertainty. The minimum k_H-value of 0.37 is found for the ternary system with relative mass fraction of PS of 0.25. This may interpreted in terms of negative deviations of k_H-values for immiscible polymer pairs, as described above. There is no indication for the occurrence of self-association effect. However, we have found excessively large values for Huggins' constants, k_H, in binary PAMA/xylene systems, and some of the corresponding ternary systems. These are characteristic for systems exhibiting self-association of PAMA component, as confirmed by our previous results [11], but also by other authors' findings [21,22].

The influence of the self-association of polymeric molecules on the solution viscosity is reflected in the experimental values of miscibility criterion variables. The b_{12}, $\Delta b^{*}_{\rm rel}$ and $\Delta b^{**}_{\rm rel}$ values for all investigated systems are given in Table 4. In all of the investigated systems negative deviations of Huggins' slopes are observed, producing negative $\Delta b^{*}_{\rm rel}$ and $\Delta b^{**}_{\rm rel}$-values, pointing to the immiscibility (repulsive interaction) of investigated polymer pairs. In systems exhibiting no self-association, the b_{12}-value (and related $\Delta b^{*}_{\rm rel}$ and $\Delta b^{**}_{\rm rel}$ values) should be independent on the polymer blend composition. However, the data show that a significant compositional variation in miscibility criterion variables is obtained for all the investigated ternary systems. Since no self-association is expected to occur in the PS/EPC/xylene system, one has to take into account at least one additional effect that may induce the compositional variation of b_{12}-value. According to the literature [23,26], that effect originates from the polymer–solvent interactions (solvent power decreases with the molar mass increase). Since average polymer molar mass changes with the polymer mixture composition, a strong dependence of b_{12} on average molar mass of polymer mixture is observed in many systems studied [26].

In conclusion, the miscibility data obtained by thermodynamical calculations in polymer blends cannot be simply transferred to the dilute polymer solution region. On the other hand, independent viscosity measurements, like those described in this article give clearer picture of the interactions in

Table 4
Miscibility criterion variables for investigated ternary systems

	PS/EPC			PS/PDDMA			PS/PODMA		
w(PS)	b_{12}	$\Delta b^{*}_{\mathrm{rel}}$	$\Delta b^{**}_{\mathrm{rel}}$	b_{12}	$\Delta b^{*}_{\mathrm{rel}}$	$\Delta b^{**}_{\mathrm{rel}}$	b_{12}	$\Delta b^{*}_{\mathrm{rel}}$	$\Delta b^{**}_{\mathrm{rel}}$
0.25	1182	−0.47	−0.50	1361	−0.45	−0.45	1852	−0.11	−0.25
0.5	3033	−0.87	−0.88	424	−0.83	−0.83	451	−0.67	−0.72
0.75	3255	−1.36	−1.34	1576	−0.37	−0.37	−1254	−1.92	−1.77
	$b^{*}_{12} = 3518,\ b^{**}_{12} = 3719$			$b^{*}_{12} = 2492,\ b^{**}_{12} = 2493$			$b^{*}_{12} = 1368,\ b^{**}_{12} = 1629$		

All b_{12}-values in cm^{6}g^{-2}.

ternary polymer solutions of the polymer 1/polymer 2/solvent type.

5. Concluding remarks

In this work, miscibility and molecular interactions in three polymer mixtures composed of polystyrene and poly(ethylene-co-propylene), polystyrene and poly(dodecyl methacrylate) as well as polystyrene and poly(octadecyl methacrylate) were investigated. All the mixtures were studied by calculation, in binary polymer blends, and experimentally, in dilute xylene solutions.

The group contribution approach was used to estimate the miscibility behavior in binary blends. All the investigated polymer pairs were predicted to be immiscible. The strength of repulsive interactions leading to immiscibility was found to increase in the order: PS/PDDMA < PS/PODMA < PS/EPC.

The interactions in dilute xylene solutions at 30 °C were studied by the dilute solution (capillary) viscometry method. All investigated polymer/polymer binaries showed negative viscometric interaction parameter values ($\Delta b^{*}_{\mathrm{rel}}, \Delta b^{**}_{\mathrm{rel}} < 0$). The occurrence of repulsive interactions between polymeric components was deduced to confirm the calculations in solid blends.

The self-association of PAMA molecules significantly affected the viscosity of investigated dilute binary and ternary polymer solutions, as supported by two experimental findings. At first, high values of Huggins' constants, k_{H}, were found in both investigated binary PAMA/xylene solutions. At second, experimental Δb_{12} values were found to be dependent on the polymer mixture composition.

Dilute solution viscosity was proved to be the method-of-choice for qualitative study on interactions in ternary polymer solutions of the polymer 1/polymer 2/solvent type.

References

[1] Flory PJ. Principles of polymer chemistry. London: Cornell University Press; 1953.
[2] Mortimer R, Orszulik S. Chemistry and technology of lubricants. London: Balckie Academic & Professional; 1977.
[3] Ver Strate G, Struglinski MJ. Polym Mater Sci Eng 1989;61:252.
[4] Benfaremo N, Liu C. Lubrication 1990;76:1.
[5] Shulz D, Glass J. Polymers as rheology modifiers. Washington: ACS Ser 462; 1991.
[6] Sen A, Rubin ID. Macromolecules 1990;23:2519.
[7] Janović Z, Jukić A. Rheological properties and miscibility of poly(alkyl methacrylate) and polyolefine lubricating oil mixed additive. In: Bartz WJ, editor. Proceedings of the 14th international colloquium tribology and lubrication engineering, 1. p. 155.
[8] Jukić A, Tomašek LJ, Janović Z. Lubr Sci 2005;17:431.
[9] Janović Z, Sarić K, Sertić-Bionda K. Chem Biochem Eng Q 1998;12:19.
[10] Vidović E, Sarić K, Janović Z. Croat Chem Acta 2002;75:769.
[11] Jukić A, Rogošić M, Bolarić I, Tomašek LJ, Janović Z. J Mol Liq 2004;112:161.
[12] Coleman MM, Graf JF, Painter PC. Specific interactions and miscibility of polymer blends. Lancaster: Technomic; 1991.
[13] Chee KK. Eur Polym J 1990;26:423.
[14] Kent MS, Tirell M, Lodge TP. Macromolecules 1992;25:5383.
[15] Mathew M, Ninan KN, Thomas S. Polymer 1998;39:6235.
[16] Abdel-Azim A, Atta A, Farahat M, Butros W. J Appl Polym Sci 1998;69:1471.
[17] Rogošić M, Mencer HJ. Eur Polym J 1997;33:621.
[18] Krigbaum WR, Wall FT. J Polym Sci 1950;5:505.
[19] Catsiff EH, Hewett WA. J Appl Polym Sci 1962;6:S30.
[20] Philippoff WE. Ber Dtsch Chem Ges 1937;70:827.
[21] Bohdanecký M, Kovář J. Viscosity of polymer solutions. Amsterdam: Elsevier; 1982.
[22] Lewandowska K, Staszewska DU, Bohdanecký M. Eur Polym J 2001;37:25.
[23] Cragg LH, Bigelow CC. J Polym Sci 1955;16:177.
[24] ten Brinke G, Karasz FE, MacKnight WJ. Macromolecules 1983;16:1827.
[25] ten Brinke G, Karasz FE. Macromolecules 1984;17:815.
[26] Böhmer B, Berek D, Florián Š. Eur Polym J 1970;6:471.