Hydrodynamic Properties of Polymer Mixtures in Solution[†]

Cristina-Eliza Brunchi, Maria Bercea,* and Simona Morariu

"Petru Poni" Institute of Macromolecular Chemistry, 41-A Grigore Ghica Voda Alley, 700487 Iasi, Romania

The paper investigates the hydrodynamic properties of polyacrylonitrile (PAN) and poly(*N*-(4-carboxyphenyl)maleimide) (PMI) solutions in dimethylformamide (DMF) in comparison with PMI/PAN/DMF ternary mixtures. The experimental data obtained by viscometry have been discussed by means of two methods: first, the plots obtained with the classical Huggins equation are analyzed, and in parallel, an evaluation of the parameters given by the new Wolf model is presented. The experimental data obtained for binary polymer/solvent and ternary polymer/polymer/solvent mixtures fit well with this last method and allow the calculation of intrinsic viscosities and other hydrodynamic parameters, which provide new information about the competition between different types of interactions for polymer mixtures in solution. The compatibility of the two polymers dissolved in a common solvent is also discussed on the basis of two parameters: Δb and α, reflecting the interactions between the polymer segments and polymer/polymer miscibility, respectively. The sign of these parameters shows that the PMI/PAN blends in DMF are miscible in the range of PAN mass fraction between 0.36 and 0.75.

Introduction

The viscometric behavior of polyacrylonitrile (PAN) solutions was investigated in different concentration regimes: extremely dilute, dilute, and semidilute.[1,2] In dilute polymer solution, the reduced viscosity is proportional to concentration, as indicated by the Huggins equation. The viscosity of a polymer solution in the extremely dilute region usually reveals some abnormalities such as the curves of reduced viscosity (η_{sp}/c) plotted against concentration that show either an upward or a downward turn as the concentration is below a definite concentration.[1−4] The experimental works encounter some difficulties at such low concentrations of polymer because systematic errors appear in the evaluation of the intrinsic viscosity ($[\eta]$), being originated from the improper technique by which the viscosity of polymer solution is determined at very low concentrations. Upward changes in the slope of η_{sp}/c as a function of concentration were reported for polyelectrolytes due to the fact that electrostatic repulsion between the charged groups of the macromolecules strongly increases upon dilution.[5]

Despite considerable efforts, the understanding of the anomalous viscosity behavior of neutral polymer solutions at low concentrations is still far from complete. In the case of PAN solutions, such behaviors were attributed either to the polymer losses caused by the adsorption of the polymer molecules on the walls of the viscometer which decreases considerably the effective diameter of the viscometer capillary, either to an expansion of the individual coils, drainage, kinetic energy effects, or conformational changes of the macromolecules in solution.[1,2]

Many efforts were carried out to obtain a reliable equation for determining the intrinsic viscosity by using the viscometric data obtained at different concentrations. A brief presentation of the most important methods and their applicability limits is recently published.[5] A new phenomenological approach was proposed as an alternative method for the determination of the intrinsic viscosity for the polyelectrolytes, in the presence and in the absence of salts.[6,7] The value of $[\eta]$ is determined from the initial slope of the dependence of ln η_{rel} (where η_{rel} is the relative viscosity) as a function of concentration at sufficiently low shear rates and polymer concentrations. This model has been successfully applied for salt-free aqueous solutions of poly(*N*-butyl-4-vinylpyridinium bromide) samples with different quaternization degrees[6] and sodium polystyrene sulfonate,[7] as well as for a salted solution of sodium polystyrene sulfonate,[6] cationic polysaccharides based on dextran in salt-free aqueous solution, and water−methanol mixtures.[8] We obtained previously accurate values of the intrinsic viscosity by applying the new model for neutral polymers in solution, that is, PAN in dimethylformamide (DMF).[9]

The polymers containing *N*-substituted maleimides, such as poly(*N*-(4-carboxyphenyl)maleimide) (PMI), exhibit special properties due to the rigid imide rings in the backbones. Thus, *N*-phenylmaleimide polymers are used in some electro-optical applications which requires the improvement of the thermal stability, processability, electro-optical coefficients, and optical loss.[10−12] These properties are related to each other, and the enhancement of one property often adversely affects other properties. For example, rigid polymers with high glass transition temperatures usually have some difficulties in processing.

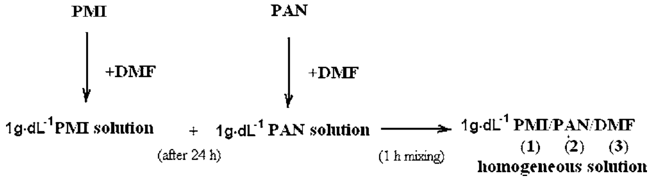
The above-mentioned conflicting properties can be optimized by using the copolymerization technique[13,14] which enables us to control the concentrations of the hard and soft segments as well as the chromophores. Also, the polymer blends are extensively investigated because of their growing interest for practical applications. Blends are an inexpensive way to improve the polymer properties, producing desirable materials without the effort of devising a new synthesis. In some cases, by synergistic effects, such combinations may possess unique properties that are different from those of individual components. However, the superior properties of polymer blends are determined by the miscibility of homopolymers on the molecular scale.

[†] Part of the "Sir John S. Rowlinson Festschrift".

* To whom correspondence may be addressed. E-mail: bercea@icmpp.ro. Tel.: +40 232 217454. Fax: +40 232 211299.

10.1021/je1005714

Scheme 1. Preparation of the PAN/PMI/DMF Ternary Systems



The polymer mixtures in solution often exhibit properties that are superior to each individual polymer component. The purpose of the present work is to investigate the hydrodynamic behavior of solutions of neutral polymer mixtures, that is, PMI/PAN mixtures, and to obtain information concerning the interactions exhibited in a common solvent (DMF) and about the compatibility of PMI/PAN at different mass ratios of PMI and PAN. Viscometry is very often used to determine the degree of compatibility among the polymeric components for a mixture of polymers in solution. The basic idea is to measure the viscosity of the ternary polymer systems consisting of polymer (1)/polymer (2)/solvent (3) and is based on the assumption that the mutual interactions of macromolecules in solution will significantly change the viscosities and other hydrodynamic parameters relative to those of the binary systems polymer (1)/solvent (3) and polymer (2)/solvent (3). Generally, favorable interactions cause positive deviations, and unfavorable interactions determine negative deviations from the additive rule with respect to the polymer composition.

Experimental Section

Materials. PAN under study was synthesized by radical polymerization in toluene using 2,2′-azobisisobutyronitrile as the initiator at $T = 333$ K. The resulting samples were filtered and purified by dissolution in DMF, followed by precipitation in methanol, and then dried under reduced pressure at room temperature. The samples were submitted to fractionation by using DMF−methanol as solvent−precipitant systems.

N-(4-Carboxyphenyl)maleimide was obtained by the reaction between the maleic anhydride and the *p*-aminobenzoic acid, in dried acetone, at ambient temperature, followed by chemical cyclodehydration.[15] PMI was obtained by radical polymerization of *N*-(4-carboxyphenyl)maleimide in methyl ethyl ketone using 2,2′-azobisisobutyronitrile as an initiator at $T = 343$ K. The resulting sample was precipitated in methanol and then dried under reduced pressure at room temperature.

The molecular weights were determined by gel permeation chromatography (GPC) using a PL-EMD 950 evaporative mass detector. The column system was thermostatted at $T = 298$ K. Calibration was done using standard polystyrene with narrow polydispersity. The samples were eluted with DMF, and the flow rate was 0.7 $\text{mL}\cdot\text{min}^{-1}$. The volume of the injected polymer solutions was always 20 μL. For the present study we selected a PAN sample with $M_w = 3.5\cdot10^4$ $\text{g}\cdot\text{mol}^{-1}$ and $M_w/M_n = 1.2$ and a PMI sample with $M_w = 8\cdot10^3$ $\text{g}\cdot\text{mol}^{-1}$ and $M_w/M_n = 1.3$.

Sample Preparation. In the present paper, when we refer to the PMI/PAN binary mixture, the index 1 corresponds to PMI, whereas the index 2 corresponds to PAN. Thus w_2 represents the PAN weight fraction in the polymer mixture. The ternary PMI/PAN/DMF systems were prepared as shown in Scheme 1. Homogeneous solutions of 1 $\text{g}\cdot\text{dL}^{-1}$ PAN and 1 $\text{g}\cdot\text{dL}^{-1}$ PMI were prepared in DMF and kept 24 h at room temperature. Solutions of PMI/PAN/DMF ternary mixtures with different weight fractions of PAN (w_2) in the polymer mixture were prepared by mixing the two homogeneous solutions to obtain different weight fractions of PAN, w_2: 0, 0.10, 0.25, 0.50, 0.75, 0.90, and 1.

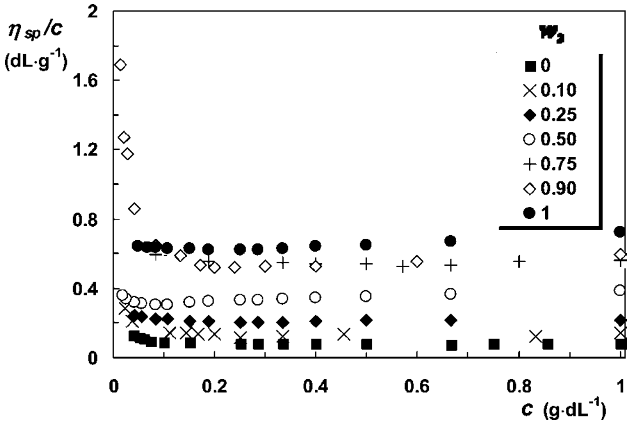


Figure 1. Plots of the reduced viscosity as a function of concentration of PMI, PAN, and PMI/PAN mixtures for different w_2 values (in DMF, $T = 298$ K).

Viscometry. The viscometric measurements were carried out in DMF at $T = 298$ K with an Ubbelohde suspended-level viscometer. The kinetic energy corrections were found to be negligible. The flow time for the solvent was 166.25 s. The flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ± 0.02 %.

Results and Discussion

The intrinsic viscosity, $[\eta]$, is usually evaluated from the viscosity measurements at finite concentration by using the extrapolation methods to infinite dilution. The most popular method is the Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta]_H + k_H[\eta]_H^{\ 2}c \qquad (1)$$

k_H is referred to as the Huggins dimensionless constant and relates to the size and shape of polymer segments, as well as to the hydrodynamic interactions between different segments of the same polymer chain; η_{sp} represents the specific viscosity ($\eta_{sp} = \eta_{rel} - 1$), which reflects the fractional change in viscosity produced by the addition of the solute, and η_{rel} is the relative viscosity showing the change in viscosity, usually expressed as a ratio between the viscosity of the polymer solution and the viscosity of the solvent.

The η_{sp}/c versus c dependences for PAN, PMI, and PMI/PAN mixtures in DMF at $T = 298$ K are given in Figure 1.

The values of $[\eta]_H$ and k_H obtained for the samples in the dilute region (for which $1.2 < \eta_{rel} < 1.9$) are given in Table 1. It can be observed that k_H changes as a function of composition of the PMI/PAN mixture. Also, in the region of low polymer concentrations (for which the values of the relative viscosity are much lower than 1.2) the reduced viscosity deviates upward from linearity. Such positive deviations from the linear behavior in the dependences of η_{sp}/c versus concentration were previously reported for PAN.[1,2]

Recently, a new alternative method[6,7] was proposed for the determination of the intrinsic viscosity from the initial slope of the dependence of ln η_{rel} as a function of c at sufficiently low

Table 1. Viscometric Parameters for PMI/PAN Mixtures in DMF at $T = 298$ K

w_2	$[\eta]_H$ (eq 1) dL·g^{-1}	k_H (eq 1)	$[\eta]_W$ (eq 2) dL·g^{-1}	error dL·g^{-1}	B (eq 2)	k_H (eq 4)	Δb	α
0.00	0.0793	0.5420	0.0794	0.0011	−0.39703	0.8970		
0.10	0.1248	0.1798	0.1333	0.0070	1.08629	0.0186[a]	−0.056	−0.593
0.25	0.2217	0.2399	0.2062	0.0028	0.25446	0.2455	−0.026	−0.226
0.50	0.3232	0.5797	0.3169	0.0023	−0.08066	0.5807	0.028	0.190
0.75	0.4784	0.3766	0.4850	0.0149	0.15991	0.3401	0.008	−0.017
0.90	0.5004	0.3914	0.5137	0.0237	0.20302	0.2970	−0.126	−0.048
1.00	0.5851	0.3876	0.5923	0.0024	0.16097	0.3390		

[a] Value adjusted by taking into account the fitting errors.

shear rates and polymer concentrations, according to the following equation:

$$\ln \eta_{\mathrm{rel}} = \frac{c[\eta]_{\mathrm{W}} + Bc^2[\eta]_{\mathrm{W}}[\eta]^{\bullet}}{1 + Bc[\eta]_{\mathrm{W}}} \tag{2}$$

where B represents a system specific constant correlated with the Huggins constant:

$$k_{\mathrm{H}} = \frac{1}{2} - \left(1 - \frac{[\eta]^{\bullet}}{[\eta]}\right)B \tag{3}$$

which holds true for the range of pair interactions between the solute,[16] and $[\eta]^{\bullet}$ is the characteristic specific hydrodynamic volume.

Equation 2 was successfully verified for different polyelectrolyte solutions[6−8,16,17] as well as for neutral polymers.[9] For uncharged polymers we found that $[\eta]^{\bullet}$ is zero, as theoretically predicted,[18] and in this case, the Huggins constant can be expressed as:

$$k_{\mathrm{H}} = \frac{1}{2} - B \tag{4}$$

For $B = 0$, which means there is no curvature in the plot of ln η_{rel} versus c, one obtains $k_{\mathrm{H}} = 0.5$ (weak polymer−solvent interactions). B is positive for almost uncharged polymers when the relative increase in viscosity slows down as the polymer concentration rises,[16] typical for thermodynamically good solvents.

We apply eq 2 for PMI, PAN, and PMI/PAN mixtures in DMF at $T = 298$ K (Figure 2). The difficulties encountered in a clear extrapolation of the reduced viscosity to zero polymer concentration can be avoided by using this new method which gives linear dependences, including the region of very low polymer concentration. The $[\eta]_{\mathrm{W}}$ and B parameters were determined by fitting the experimental dependences of ln η_{rel} versus c, and the obtained values are given in Table 1. One can observe that the resulting errors in determining the $[\eta]_{\mathrm{W}}$ values are relatively small and the experimental uncertainties remain below 3 %, except for two samples having the composition in the vicinity of pure polymer (the values obtained for $[\eta]_{\mathrm{w}}$ corresponding to w_2 of 0.1 and 0.9 are 0.1333 dL·g^{-1} ± 5.27 % and 0.5137 dL·g^{-1} ± 4.62 %, respectively). Also, for all binary and ternary systems investigated in the present paper, we have found $[\eta]^{\bullet} = 0$.

The favorable polymer−solvent interactions can be translated in high B values (Figure 3) or low k_{H} values (Figure 4). It can be observed that the highest errors in determining the B values are obtained for the high content of PMI. However, the maximum in the curve given in Figure 3 is clearly evidenced even by taking into account these errors.

By further increasing the PAN content in the binary polymer mixture, B decreases and reaches a value close to those determined for the PAN solutions (free of PMI).

Figure 4 gives a comparative plot of the Huggins constant determined from the experimental data given in Figure 1 and k_{H} calculated from the parameter B (eq 2). The evolution of k_{H} as a function of w_2 is similar in both cases. The most significant difference is observed for $w_2 = 0.10$ for which the error in determining B was also high. Usually, the values of k_{H} are in the range of 0.3 (good polymer−solvent interactions) to 0.5 (poor polymer−solvent interactions). The k_{H} values between 0.8 and 1.3 were found in the case of aggregated molecules.[19]

For multicomponent polymer systems, the dependence of k_{H} on the composition is more complex, being influenced by the

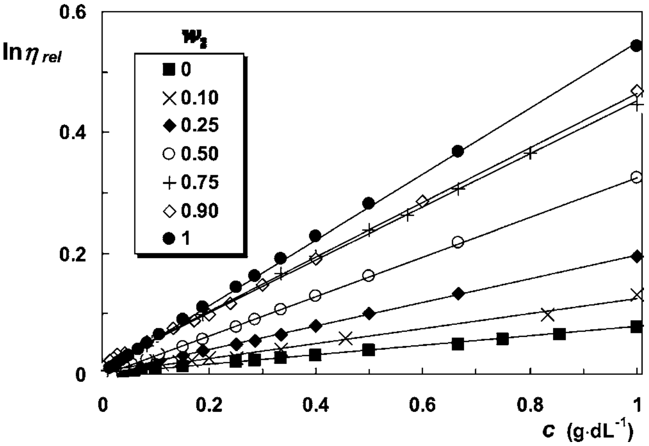


Figure 2. Plots of ln η_{rel} as a function of concentration of PMI, PAN, and PMI/PAN mixtures in DMF at $T = 298$ K for different w_2 values.

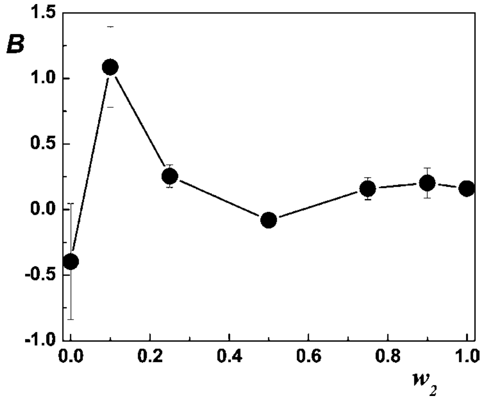


Figure 3. Dependence of the parameter B from eq 2 as a function of composition of the PMI/PAN binary mixture, w_2.

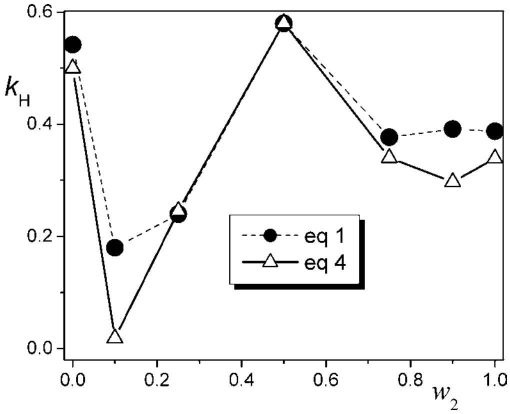
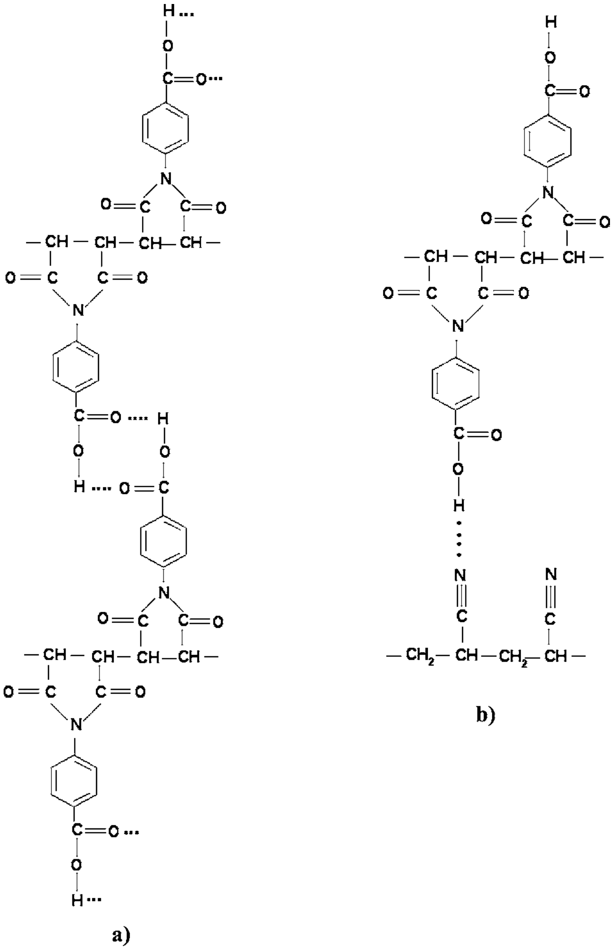


Figure 4. Dependence of the experimental and calculated k_H values as a function of PMI/PAN binary composition.

Scheme 2. Schematic Representation of the Possible H-Bond between Polymers in DMF (a) in Excess of PMI and (b) around $w_2 = 0.50$



conformational changes of each type of polymer with mixing as well as by the thermodynamic or hydrodynamic interactions among polymers. In our case, for two particular systems at $w_2 = 0$ and $w_2 = 0.50$, the Huggins constant is higher than 0.5 (corresponding to negative B values, Table 1), indicating poor interactions between the polymer coils and the solvent.

The values of B and k_H obtained for the PMI/DMF binary mixture ($w_2 = 0$) suggest the existence of macromolecular aggregates as a result of the formation of hydrogen bonds between the PMI chains as shown in Scheme 2a. These aggregates are destroyed by the addition of new PAN chains, and the interactions between each polymer and DMF become predominant. When the weight ratio of the two polymers in the ternary mixture approaches unity, the interactions between PMI and PAN chains intensify due to the H-bonds established between $-C{\equiv}N$ and $-COOH$ from PAN and PMI chains, respectively (Scheme 2b). At high PAN concentrations in the ternary mixture, the interactions between PAN chains become favorable.

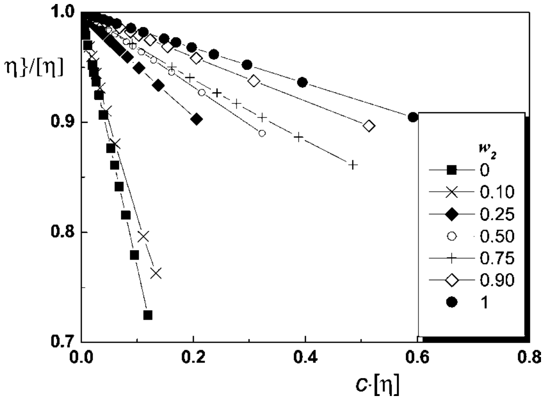


Figure 5. Reduced specific hydrodynamic volume as a function of the reduced polymer concentration for different weight fractions of PAN in the polymer−polymer binary mixture.

To interpret the viscosity data, some parameters were also introduced, such as: $\{\eta\}$ = the specific hydrodynamic volume at a given polymer concentration, c: $\{\eta\} = (\partial \ln \eta/\partial c)_{T,p,\dot{\gamma}}$. Thus, the intrinsic viscosity represents the specific hydrodynamic volume of isolated polymer coils:[7]

$$\lim_{\substack{c\to 0\\ \dot{\gamma}\to 0}} \{\eta\} = [\eta]$$

The ratio between the specific hydrodynamic volume at a given polymer concentration c and that at infinite dilution, $\{\eta\}/[\eta]$, provides information on the changes in the hydrodynamic volume of an individual macromolecules induced by the presence of other polymers. The value of this ratio can be obtained from the equation:

$$\frac{\{\eta\}}{[\eta]} = \frac{1 + 2Br(c[\eta]) + B^2r(c[\eta])^2}{1 + 2B(c[\eta]) + B^2(c[\eta])^2} \tag{5}$$

where $r = ([\eta]^{\bullet}/[\eta])$ and $c[\eta]$ = a dimensionless reduced concentration.

For $[\eta]^{\bullet} = 0$ (neutral polymers), eq 5 is reduced to:

$$\frac{\{\eta\}}{[\eta]} = \frac{1}{1 + 2B(c[\eta]) + B^2(c[\eta])^2} \tag{6}$$

Figure 5 shows the dependences obtained by means of eq 6 and the parameters given in Table 1 for the PMI, PAN, and PMI/PAN mixtures in DMF solutions.

All dependences are linear and start from $\{\eta\}/[\eta] = 1$ at $c[\eta] = 0$ when the specific hydrodynamic volume $\{\eta\}$ becomes equal to $[\eta]$. For the same $c[\eta]$ value, the reduced specific hydrodynamic volume given by the $\{\eta\}/[\eta]$ ratio increases with increasing the PAN content in the mixture, and this can be due to differences in the molecular weight between PAN and PMI as well as to solvent quality for each polymer.

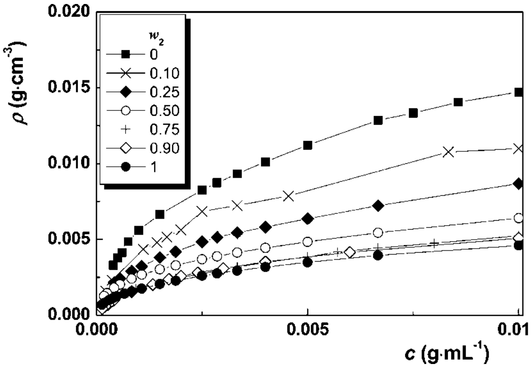


Figure 6. Variation of the coil density with polymer concentration for PMI/PAN samples in DMF at $T = 298$ K.

The viscometric data can be also used to estimate the coil density of the polymer chains in solution by using the method proposed by Qian et al.[20,21] according to the following equation:

$$\rho = \frac{c}{\eta_{sp}}(1.25 + 0.5\sqrt{56.4\eta_{sp} + 6.25}) \tag{7}$$

Figure 6 shows the concentration dependence of the coil density by using the experimental data from Figure 1 by means of eq 7.

One observes that PMI, for which the smallest reduced specific hydrodynamic volume (Figure 5) was obtained, presents the highest coil density due to the aggregation attributed to both intra- and intermolecular interactions. For increasing content of PAN in the mixture, the reduced specific hydrodynamic volume increases, and the density decreases.

The data obtained by viscometry (viscosity, Huggins coefficient) allow the calculation of some parameters that give information concerning the miscibility of two polymers in a common solvent. Krigbaum and Wall[22] have proposed the following form for the classical Huggins equation that can be applied to polymer mixtures in a common solvent:

$$\eta_{spm} = [\eta]_m c_m + b_m {c_m}^2 \tag{8}$$

where η_{spm} is the specific viscosity of a polymer mixture in solution, $[\eta]_m$ is the intrinsic viscosity of the polymer mixture, and c_m represents the total concentration of polymer in solution. b_m ($b_m = k_m[\eta]_m{}^2$ where k_m is the Huggins coefficient of the polymer blend) reflects the binary interactions between polymer segments. The compatibility criterion proposed by Krigbaum and Wall,[22] Δb, is defined as:

$$\Delta b = b_{12}^{exp} - b_{12}^{id} \tag{9}$$

b_{12} is a parameter that reflects the interactions between different polymer molecules.

The experimental value b_{12}^{exp} can be obtained from the following relationship:

$$b_m^{exp} = b_{11}{w_1}^2 + b_{22}{w_2}^2 + 2b_{12}^{exp}w_1w_2 \tag{10}$$

where b_{11} and b_{22} are self-interaction parameters obtained from the slopes of η_{sp}/c versus concentration for the pure polymers in solution and w_1 and w_2 represent the mass fractions of PMI and PAN, respectively, in the polymer mixture.

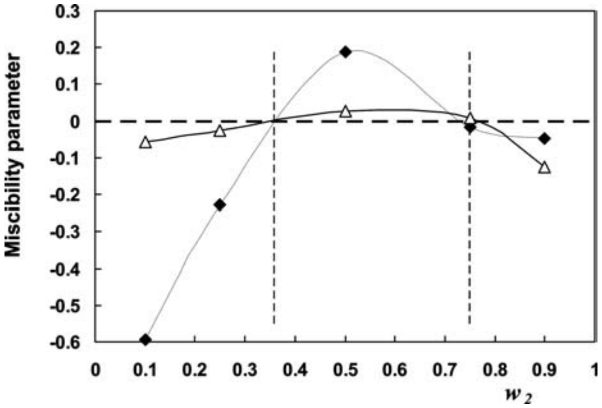


Figure 7. Plots of the miscibility parameters vs weight fraction of PAN in the polymer−polymer binary mixture.

b_{12}^{id} is given by the following equation:

$$b_{12}^{id} = \sqrt{b_{11}b_{22}} \tag{11}$$

Thus, two polymers are considered compatible if $\Delta b > 0$ (attractive interactions) and incompatible if $\Delta b < 0$ (immiscibility and phase separation).[22,23]

Sun et al.[24] proposed a thermodynamic parameter α to predict the polymer/polymer miscibility defined as:

$$\alpha = k_m - \frac{k_1(w_1[\eta]_1)^2 + k_2(w_2[\eta]_2)^2 + 2(k_1k_2)^{0.5}[\eta]_1[\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{12}$$

where k_1, k_2, and k_m are the Huggins constants for PMI, PAN, and the blend, respectively.

The positive sign of the parameter α indicates a good miscibility of the polymer mixture, and the negative sign of α suggests that the polymer mixture is immiscible.[23−25]

The values of Δb and α parameters calculated with eqs 9 and 12, respectively, are given in Table 1. Negative values for both parameters can be observed for $w_2 < 0.36$ and $w_2 > 0.75$, suggesting that the polymers are immiscible on these mass fraction ranges, when the polymer−solvent interactions and the interactions between the segments which belong to the same macromolecular chain are favorable. The compatibility between PMI and PAN was found to increase in the composition range $0.36 < w_2 < 0.75$ (Figure 7). These observations are in agreement with those obtained from the analysis of B and k_H parameters.

By analyzing the composition dependence of the intrinsic viscosity given in Figure 8, within the limits of the method errors (Table 1), one can consider that $[\eta]_W$ obeys the additive rule given in a general form in eq 13:

$$\eta_m^{id} = w_1\eta_1 + w_2\eta_2 \tag{13}$$

Here, η_1 and η_2 refer to the viscosities of polymer−solvent binary systems.

The specific viscosity of a ternary polymer (1)/polymer (2)/solvent (3) system may deviate from the ideal value given by eq 13. These deviations are attributed to the effect of thermodynamic interactions of the two polymers in the solution.[26] If a

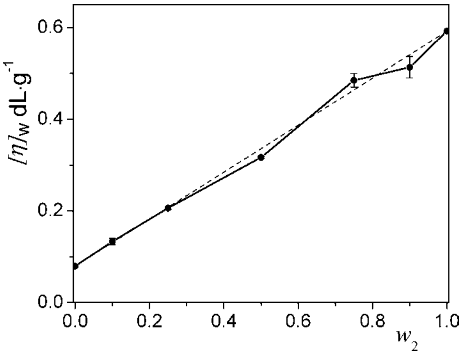


Figure 8. Plot of $[\eta]_W$ vs w_2: full line, experimental dependence; dotted line, additive rule (eq 13).

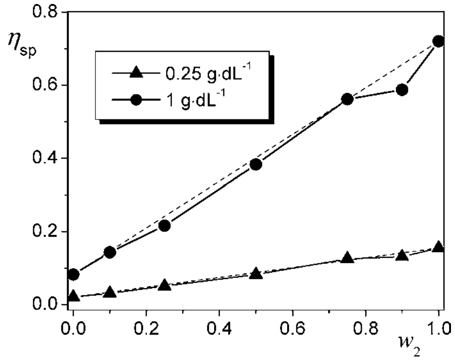


Figure 9. Dependence of the specific viscosity as a function of w_2 for two polymer concentrations: full lines, experimental dependence; dotted lines, additive rule (eq 13).

positive deviation is found, the two polymers are considered to be compatible, and heterogeneous contacts (segments of polymer 1/segments of polymer 2) are preferred over homogeneous contacts (segments of the same polymer). When the macromolecular coils in solution tend to uncoil to a certain extent, the available area for the occurrence of the heterogeneous contacts increases, determining a higher value of the viscosity as compared with its ideal value, η_m^{id}, obtained by the additive rule. If a negative deviation is observed, the average dimensions of the macromolecular coils decrease due to the repulsive interactions between different polymer segments. Thus, a value of the viscosity much lower than η_m^{id} is considered a sign for the incompatible polymer mixture.[26,27] From Figure 9 it can be observed that the deviation of the experimental data from η_m^{id} becomes more important as the polymer concentration increases. According to the criterion based on the viscosity, PMI/PAN mixtures are immiscible over a large domain of composition, and the minimum value obtained for $w_2 = 0.9$ suggest very small or no interaction between PMI and PAN. The small negative deviations registered for $w_2 < 0.7$, suggesting that the polymers are immiscible in this concentration range, are in contradiction with the data obtained at the same concentration of PAN when the parameters B, k_H, Δb, and α were analyzed. This disagreement could be explained by the fact that the viscometric criteria do not take into account interactions between the polymer and the solvent but attributes the miscibility of two polymers only to the specific interactions between the unlike polymer molecules.[28]

The PMI chains dissolved in a polar solvent, such as DMF or dioxane, exhibit the ability to form aggregates through hydrogen bonding.[29,30] In DMF, PMI chains present a polarized form which can be stabilized by the high dielectric constant of the solvent (38.3), determining an increase in k_H constant (respectively a decrease in B value, Table 1). Thus, the very low yield obtained in the case of homopolymerization of *N*-(4-carboxyphenyl)maleimide in polar solvents (such as DMF or dimethylsulfoxide) can be explained by the H-bond formation between the $-$COOH pendant groups of the monomer units.[31] When a small amount of PAN is introduced into the PMI/DMF solution, these intermolecular and intramolecular interactions can be destroyed by establishing some new intermolecular interactions with the polar $-$C$\equiv$N groups in competition with the polymer$-$solvent interactions which become more pronounced. The reciprocal H-bonds with the polar solvent or the polar groups of PAN disrupt the hydrogen bonds among the PMI moieties, obstructing their possible aggregation. For $0.36 < w_2 < 0.75$, some intermolecular interactions between the $-$COOH group from PMI chains and the $-$C$\equiv$N groups from PAN can also appear.

Conclusions

The analysis of the concentration dependence of the viscosities of polymer solutions in terms of ln η_{rel} as a function of concentration, according to a new method proposed by Wolf,[6] instead of the traditional Huggins plots or similar evaluations, provides a general facility to obtain the intrinsic viscosity. This method works for aqueous solutions of polyelectrolytes in the absence or presence of salt, as well as for solutions of nonionic polymers in organic solvents. The experimental data obtained for binary polymer$-$solvent and ternary polymer$-$polymer solvent mixtures fit well with the Wolf method and allow the calculation of intrinsic viscosities and other hydrodynamic parameters, which provide new information about the competition between different types of interactions for polymer mixtures in solution.

The miscibility of PMI with PAN in DMF was estimated by using two compatibility criterions: Δb and α, which discuss the compatibility between two polymers in terms of polymer$-$polymer and polymer$-$solvent interactions. The values calculated for these parameters indicate that the PMI/PAN mixture is compatible at mass fractions of PAN ranging from 0.36 to 0.75.

The evaluation of the miscibility between PMI and PAN cannot be discussed only by analyzing the deviations of the experimental values of the viscosity (intrinsic viscosity obtained at infinite dilution or specific viscosity obtained at a given concentration) because the viscometric criteria do not take into account interactions between the polymer and the solvent but attributes the miscibility of two polymers only to the specific interactions between the unlike polymer molecules.

The results obtained in the present paper demonstrate that the presence of the interactions between atoms or a group of atoms of unlike polymers is essential to obtain a miscible polymer blend. In addition, the interactions between the segments which belong to different segments of the same polymer chain can play an important role in obtaining miscible systems.

Acknowledgment

The authors are grateful to Prof. Bernhard A. Wolf from Johannes Gutenberg Universität Mainz for the useful discussions and suggestions and to CS II Dr. Camelia Hulubei from “Petru Poni” Institute of Macromolecular Chemistry, Iasi (Romania) for kindly providing *N*-(4-carboxyphenyl)maleimide. Also, the authors thank the referees for their comments.

Literature Cited

(1) Bercea, M.; Morariu, S.; Ioan, S.; Ioan, C.; Simionescu, B. C. Viscometric Study of Extremely Dilute Polyacrylonitrile Solutions. *Eur. Polym. J.* **1999**, *35*, 2019–2024.

(2) Brunchi, C. E.; Bercea, M.; Morariu, S. Studies Concerning the Behavior of Polyacrylonitrile Solutions in Dimethylformamide at Very Low Concentrations. *High Perform. Polym.* **2008**, *20*, 311–322.

(3) Yang, H.; Yan, Y.; Zhu, P.; Li, H.; Zhu, Q.; Fan, C. Studies on the Viscosity Behavior of Polymer Solutions at Low Concentrations. *Eur. Polym. J.* **2005**, *41*, 329–340.

(4) Cai, J.; Cheng, R.; Bo, S. Effect of Concentration Reduction due to Adsorption on the Reduced Viscosity of Polymer Solution in Extremely Dilute Concentration Regime. *Polymer* **2005**, *46*, 10457–10465.

(5) Morariu, S.; Brunchi, C. E.; Ghimici, L.; Bercea, M. Viscometric Behavior of Polymer Solutions. In *Functional Polymeric Materials Designed for High Tech Applications*; Nechifor, M., Ed.; SIGNPOST: Trivandrum, India, 2010; pp 85−107.

(6) Wolf, B. A. Polyelectrolyte Revisited: Reliable Determination of Intrinsic Viscosity. *Macromol. Rapid Commun.* **2007**, *28*, 164–170.

(7) Eckelt, J.; Knopf, A.; Wolf, B. A. Polyelectrolytes: Intrinsic Viscosity in the Absence and in the Presence of Salts. *Macromolecules* **2008**, *41*, 912–918.

(8) Ghimici, L.; Nichifor, M.; Wolf, B. A. Ionic Polymers Based on Dextran: Hydrodynamic Properties in Aqueous Solutions and Solvent Mixtures. *J. Phys. Chem. B* **2007**, *113*, 8020–8025.

(9) Brunchi, C. E.; Bercea, M.; Morariu, S. Viscometric and Rheological Study of Polyacrylonitrile Solutions. *e-Polym.* **2009**, *065*, 1–10.

(10) Oishi, T.; Sase, K.; Tsutsumi, H. Synthesis and Thermostabilities of *N*-[4-(*N′*-Substituted Aminocarbonyl)phenyl]maleimide Polymers. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 2001–2012.

(11) Hulubei, C.; Morariu, S. Synthesis and Radical Polymerization of *N*-(3-acetyl-4-carboxy-phenyl)-maleimide. *High Perform. Polym.* **2000**, *12*, 525–533.

(12) Morariu, S.; Bercea, M.; Hulubei, C. Rheological Investigation of Some Copolymers of N-(substituted maleimide) with Styrene in Dimethylsulfoxide. *J. Macromol. Sci., Phys.* **2008**, *47*, 1108–1116.

(13) Hulubei, C.; Morariu, S. Functional Copolymers of *N*-(4-formylphenoxy-4-carbonylphenyl)maleimide with Styrene. *High Perform. Polym.* **2000**, *12*, 367–375.

(14) Morariu, S.; Hulubei, C. Radical Copolymerization of Functional *N*-substituted maleimides with *N*-vinyl-2-pyrrolidone. *High Perform. Polym.* **2006**, *18*, 185–198.

(15) Mikroyannidis, J. A. Crosslinkable Aromatic Polyketones with Maleimide Pendant Groups. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 669–677.

(16) Samadi, F.; Wolf, B. A.; Guo, Y.; Zhang, A.; Dieter Schlüter, A. Branched versus Linear Polyelectrolytes: Intrinsic Viscosities of Pherically Charged Dendronized Poly(methyl methacrylates) and Their Uncharged Analogues. *Macromolecules* **2008**, *41*, 8173–8180.

(17) Badiger, M. V.; Gupta, N. R.; Eckelt, J.; Wolf, B. A. Intrinsic Viscosity of Aqueous Solutions of Carboxymethyl Guar in the Presence and in the Absence of Salts. *Macromol. Chem. Phys.* **2008**, *209*, 2087–2093.

(18) Wolf, B. A. Johannes Gutenberg University Mainz, Germany. Personal communication, 2010.

(19) Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds. *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.

(20) Qian, J. W.; Rudin, A. Prediction of Hydrodynamic Properties of Polymer Solutions. *Eur. Polym. J.* **1992**, *28*, 733–738.

(21) Qian, J. W.; Wang, M.; Han, D. L.; Cheng, R. S. A Novel Method for Estimating Unperturbed Dimension $[\eta]_\theta$ of Polymer from the Measurement of Its $[\eta]$ in a Non-theta Solvent. *Eur. Polym. J.* **2001**, *37*, 1403–1407.

(22) Krigbaum, W. R.; Wall, F. T. Viscosities of Binary Polymeric Mixtures. *J. Polym. Sci.* **1950**, *5*, 505–514.

(23) Aroguz, A. Z.; Kismir, Y. Viscometric Study on the Miscibility of Polystyrene/Brominated Polystyrene Blends. *Eur. Polym. J.* **2007**, *43*, 410–415.

(24) Sun, Z. H.; Wang, W.; Feng, Z. L. Criterion of Polymer-Polymer Miscibility Determined by Viscometry. *Eur. Polym. J.* **1992**, *28*, 1259–1261.

(25) Jiang, W. H.; Han, S. J. An Improved Criterion of Polymer-Polymer Miscibility Determined by Viscometry. *Eur. Polym. J.* **1998**, *34*, 1579–1584.

(26) Rogošić, M.; Mencer, H. J. Prediction of Copolymer Miscibility by the Viscometric Method. *Eur. Polym. J.* **1997**, *33*, 621–630.

(27) Haiyang, Y.; Pingping, Z.; Feng, R.; Yuanyuan, W.; Tiao, Z. Viscometric Investigations on the Intermolecular Interactions Between Poly(methyl methacrylate) and Poly(vinyl acetate) in Various Solvents. *Eur. Polym. J.* **2000**, *36*, 21–26.

(28) Kavlak, S.; Can, H. K.; Guner, A. Miscibility Studies on Poly(ethylene glycol)/Dextran Blends in Aqueous Solutions by Dilute Solution Viscometry. *J. Appl. Polym. Sci.* **2004**, *94*, 453–460.

(29) Rodriguez, M. A.; Aubert, J. H.; McElhanonc, J. R.; Eatough, M. O. *N*-(4-Hydroxyphenyl)maleimide. *Acta Crystallogr.* **2002**, *E58*, 0742−0744.

(30) Reghunadhan Nair, C. P.; Mathew, D.; Ninan, K. H. Free Radical Copolymerization of *N*-(4-hydroxyphenyl)maleimide with Vinyl Monomers: Solvent and Penultimate Effects. *Eur. Polym. J.* **1999**, *35*, 1829–1840.

(31) Oishi, T.; Iwahara, M.; Fujimoto, M. Polymerization and Copolymerization of *N*-(4-carboxyphenyl)maleimide. *Polym. J.* **1991**, *23*, 1409–1417.

Received for review May 28, 2010. Accepted June 16, 2010. This work was supported by CNCSIS-UEFISCSU, PNII-IDEI Project, Contract No. 516/2009, code ID-980, Additional Contract No. 1/2010.

JE1005714