

# Evaluation of Compatibility of Methacrylic Copolymers by Capillary Viscometry

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Received 3 June 1999; accepted 8 December 1999

**ABSTRACT:** The estimation of the compatibility of different pairs of polymers can be based on capillary viscometry data for ternary polymer-polymer-solvent systems using mathematical models based on the slope of the Huggins equation ( $\Delta b$ ) and Huggins constant ( $\Delta k'$ ). In this study, the compatibility of binary mixtures of six types of methacrylic copolymers with similar molecular weights but different functional groups [one characterized by amine groups (EuE), two by ammonium groups (EuRL EuRS), two by carboxylic groups (EuL EuS), and one without charge (EuNE)] was evaluated using these methods. On the basis of Huggins and Kraemer constants, acetone and tetrahydrofuran were selected as good solvents for the programmed blends. Cationic copolymers mixed with anionic copolymers showed the formation of visible aggregates. The study performed on the other blends showed that EuRL and EuRS could be considered compatible with EuE; EuNE was incompatible with both EuL and EuE, EuL and EuS were incompatible between them. EuRL and EuRS could be considered compatible even if the weight ratio seems to influence the behavior of the two copolymers. The  $\Delta k'$  approach seems to be more robust than the  $\Delta b$  model. The compatibility of different pairs of methacrylic copolymers with similar molecular weights could be evaluated using capillary viscometry. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1662–1668, 2000

**Key words:** capillary viscometry; methacrylic copolymers; compatibility

## INTRODUCTION

Polymers are considered compatible when specific attractive interactions among the functional groups of the macromolecules occur. These specific interactions can be of different nature such as dipole-dipole, ion-dipole, hydrogen bonding, etc. Because of its simplicity, capillary viscometry is an attractive method for investigating the interaction of macromolecules. Some authors<sup>1,2</sup> have attempted the estimation of the compatibility of different pairs of polymers based on intrinsic

viscosity data for ternary polymer-polymer-solvent system. They based their theories on the fact that the viscosity of blends of two polymers is the sum of the values of the single components, by assuming the additivity of this property. Repulsive interactions may cause shrinkage of the coils of macromolecules so that the viscosity reached by the mixture is below the expected value. On the other hand, attractive interactions may form associates of both kinds of macromolecules and expected values of viscosity are higher than the simple addition of the values of the two different polymers.

It is well known that the intrinsic viscosity value,  $[\eta]$ , is related to the molecular weight, the structure and shape of the polymer, and to the

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*Journal of Applied Polymer Science*, Vol. 76, 1662–1668 (2000)  
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power of the solvent. The strong dependence of  $[\eta]$  on the molecular weight of a polymer represents a limit in the use of  $[\eta]$  for the evaluation of other viscometer parameters.<sup>1,3</sup> For this reason, different theoretical considerations based on the Huggins equation were developed to estimate the compatibility of two different polymers. The evaluation of polymer compatibility can be useful in pharmaceutical formulation studies, because in many cases mixtures of different polymers are used.

To design a polymeric matrix suitable for monolayer (trans)dermal therapeutic systems, in a preliminary work,<sup>4</sup> we used 10 methacrylic mixtures made of two different methacrylic copolymers, a nonadhesive copolymer used to modify the drug release and a self-adhesive copolymer. Eudragit® NE 40 D, Eudragit RL 30 D, Eudragit RS 30 D, Eudragit L 30 D, and Eudragit S 30 D—all of them aqueous dispersions of acrylic acid—were selected as nonadhesive copolymers. Plastoid® E 35 L and Plastoid L 50 were used as adhesive components. Both are aqueous polymeric systems based on methacrylic acid and containing other excipients that provide adhesive properties to the dry matrix. The polymeric component of the adhesive solutions was respectively Eudragit E 100 for the Plastoid E 35 L and Eudragit L 100 for the Plastoid L 50.

Seven of the 10 mixtures showed formation of aggregates and were therefore unsuitable for the preparation of matrices. Their behavior could not always be explained simply on the basis of the pH of the mixtures and of the presence of charge on the chain of the tested copolymer. In this study, the compatibility of these 10 types of methacrylic blends was evaluated by capillary viscometry. This approach was suggested by Cragg and Bigelow,<sup>1</sup> Krigbaum and Wall,<sup>2</sup> and verified by other authors.<sup>5-9</sup> The possibility of investigating the acrylic copolymer blends interactions with a simple technique is of extreme interest because the Eudragit copolymers, in particular the Eudragit® RL and Eudragit® RS, are widely used in the oral drug delivery systems.

## THEORETICAL CONSIDERATIONS

Using the dynamic viscosity of solution ( $\eta$ ) and that of pure solvent ( $\eta_o$ ), several dimensionless

parameters may be calculated. The relative viscosity ( $\eta_{rel}$ ) could be expressed as:

$$\eta_{rel} = \eta/\eta_o = \rho kt/\rho_o kt_o \quad (1)$$

where  $t$  and  $t_o$  are the efflux times for the polymeric solution and for the solvent respectively,  $\rho$  and  $\rho_o$  are their densities, and  $k$  is a constant that includes the viscometer characteristics. In diluted solutions  $\rho$  and  $\rho_o$  can be considered equivalent and eq. (1) becomes:

$$\eta_{rel} = t/t_o \quad (2)$$

Considering the concentration of the polymer ( $c$ ), the inherent viscosity ( $\eta_{in}$ ) can be calculated from the equation:

$$\eta_{in} = (\ln \eta_{rel})/c \quad (3)$$

The fractional increase in viscosity, due to the presence of the solute, is defined as specific viscosity ( $\eta_{sp}$ ):

$$\eta_{sp} = (\eta - \eta_o)/\eta_o = \eta_{rel} - 1 = t/t_o - 1 \quad (4)$$

Because the degree of viscosity enhancement is dependent on the amount of dissolved material as well as molecular size, a more fundamental parameter is the reduced viscosity ( $\eta_{red}$ ):

$$\eta_{red} = \eta_{sp}/c \quad (5)$$

Because specific viscosity ( $\eta_{sp}$ ) is dimensionless (being a ratio between viscosities), the reduced viscosity, as well as the inherent viscosity, has the dimension of a specific volume, which may be considered as the sum of the effective hydrodynamic volumes (EHV) of the number of molecules that make up 1 g of the polymer. When the solution is infinitely diluted, the molecules have no influence on each other and the EHV is simply the addition of the effective hydrodynamic volumes of the separate molecules.

The limit of infinite dilution of the reduced viscosity (eq. 5) represents the intrinsic viscosity  $[\eta]$  that is the EHV in this situation and characterizes the fractional increase in viscosity due to each isolated molecule of solute:

$$[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c) \quad (6)$$

At higher concentrations, the reduced viscosity ( $\eta_{\text{red}}$ ) increases because of mutual interference in the solvent's flow patterns around the solute, as expressed by the Huggins equation:

$$\eta_{\text{red}} = [\eta] + k'[\eta]^2c \quad (7)$$

Equation 7 can be illustrated as a linear plot in which the intercept is the intrinsic viscosity and the Huggins constant,  $k'$ , is a dimensionless parameter related to solvent-polymer interactions. Both parameters  $[\eta]$  and  $k'$  are indirect means of the ability of the solvent to solvate a polymer, in particular the intrinsic viscosity is an expression of the hydrodynamic interference between the polymer and the solvent, thus reflecting the ability of the solvent to swell the polymer.

The constant  $k'$  can be considered independent from the molecular weight and/or the rigidity of polymer chain, and therefore suitable for the selection of a good solvent for a particular polymer. The constant  $k'$  describes the interaction resulting only from differences in the chemical structure of the polymer and/or the nature of the solvent. A low interaction among the dissolved macromolecules, expressed by low value of  $k'$ , reflects a high solvent power for the specific polymer. Nevertheless, to obtain an accurate measure of  $[\eta]$ ,  $k'$  values in the range 0.3–0.4 are desirable.<sup>10,11</sup>

An alternative extrapolation of intrinsic viscosity is the Kraemer equation:

$$\eta_{\text{in}} = (\ln \eta_{\text{rel}})/c = [\eta] - k''[\eta]^2c \quad (8)$$

Combined application of both Huggins and Kraemer extrapolations may allow determination of the intrinsic viscosity,  $[\eta]$  with greater precision.

The specific viscosity of ideal solution mixtures of two polymers ( $\eta_{\text{sp},m}$ ) can be expressed as follows:

$$\eta_{\text{sp},m} = [\eta]_m C_m + b_m C_m^2 \quad (9)$$

where  $[\eta]_m$  is the intrinsic viscosity of the polymeric mixture of the two polymers in solution,  $C_m$  is the sum of the concentrations of the two polymers, and  $b_m$  is the parameter characterizing interaction of both polymer species.<sup>2</sup>

The parameter  $b_m$  is affected by the interaction of all the polymeric species in solution;

thus, the authors proposed a further expression obtained by relating the polymer-polymer interaction for the mixture to those of the components:

$$b_m = b_{11}w_1^2 + b_{22}w_2^2 + 2b_{12}w_1w_2 \quad (10)$$

where  $w_1$  and  $w_2$  are respectively the weight fractions of the dissolved polymer 1 and polymer 2,  $b_{ii}$  values represent the slope of the Huggins plot (eq. 7):

$$b_{ii} = k'_i[\eta_i]^2 \quad (11)$$

$b_{12}$  is defined as the interspecies interaction coefficient. This parameter depends on  $[\eta]$  and the constant  $k'$ . The value of  $b_{12}$  can be calculated theoretically by using the data of each single polymer ( $b_{12,\text{cal}}$ ), from eq. 11:

$$b_{12,\text{cal}} = (b_{11}b_{22})^{0.5} \quad (12)$$

or by the experimental data of the mixture elaborated with eq. (9) and eq. (10) ( $b_{12,\text{exp}}$ ).

The information on interactions between polymer 1 and polymer 2 can be evaluated from comparison of the experimental and the theoretical values of  $b$ : ( $b_{12,\text{exp}}$  and  $b_{12,\text{cal}}$ )

$$\Delta b = b_{12,\text{exp}} - b_{12,\text{cal}} \quad (13)$$

Negative values of  $\Delta b_{12}$  are found in systems of incompatible polymers, whereas positive values refer to attractive interaction and compatibility between the polymers. In the hypothetical case that  $\Delta b = 0$ , this would signify that chains neither interact favorably nor unfavorably.

The value of Huggins constant  $k'$  could also be a source of information on the interactions in ternary polymer-polymer-solvent systems.<sup>1</sup> The difference  $\Delta k'_m$  was defined as:

$$\Delta k'_m = k'_{m,\text{exp}} - k'_{m,\text{cal}} \quad (14)$$

where  $k'_{m,\text{exp}}$  is the Huggins constant value obtained by experimental data from eq. (7) and  $k'_{m,\text{cal}}$  is the theoretical value of the ternary system when there is no thermodynamic interaction between the molecules.  $k'_{m,\text{cal}}$  is defined by the following equation:

**Table I Composition of the Polymeric Blends (Weight Ratio)**

Series No.	Blends	$w_{EuE}$	$w_{EuRL}$	$w_{EuRS}$	$w_{EuNE}$	$w_{EuL}$	$w_{EuS}$
1	EuE/EuRL	0.30	0.70	—	—	—	—
		0.50	0.50	—	—	—	—
		0.70	0.30	—	—	—	—
2	EuE/EuRS	0.30	—	0.70	—	—	—
		0.50	—	0.50	—	—	—
		0.70	—	0.30	—	—	—
3	EuE/EuNE	0.30	—	—	0.70	—	—
		0.50	—	—	0.50	—	—
		0.70	—	—	0.30	—	—
4	EuE/EuL	0.30	—	—	—	0.70	—
		0.50	—	—	—	0.50	—
		0.70	—	—	—	0.30	—
5	EuE/EuS	0.30	—	—	—	—	0.70
		0.50	—	—	—	—	0.50
		0.70	—	—	—	—	0.30
6	EuL/EuRL	—	0.70	—	—	0.30	—
		—	0.50	—	—	0.50	—
		—	0.30	—	—	0.70	—
7	EuL/EuRS	—	—	0.70	—	0.30	—
		—	—	0.50	—	0.50	—
		—	—	0.30	—	0.70	—
8	EuL/EuNE	—	—	—	0.70	0.30	—
		—	—	—	0.50	0.50	—
		—	—	—	0.30	0.70	—
9	EuL/EuS	—	—	—	—	0.30	0.70
		—	—	—	—	0.50	0.50
		—	—	—	—	0.70	0.30
10	EuRL/EuRS	—	0.30	0.70	—	—	—
		—	0.50	0.50	—	—	—
		—	0.70	0.30	—	—	—

$$k'_{m,cal} = (k'_1[\eta]_1^2 w_1^2 + k'_2[\eta]_2^2 w_2^2 + k'_1 k'_2 [\eta]_1 [\eta]_2 w_1 w_2) / ([\eta]_1 w_1 + [\eta]_2 w_2)^2 \quad (15)$$

where  $k'_1$  and  $k'_2$  are the Huggins constant,  $[\eta]_1$  and  $[\eta]_2$  the intrinsic viscosities,  $w_1$  and  $w_2$  are weight fractions respectively of the polymer 1 and the polymer 2. If  $\Delta k'_m = 0$ , it is possible to conclude that interactions other than hydrodynamic are either nonexistent or negligible, whereas different values of  $\Delta k'_m$  indicate the existence of specific interaction forces and might provide information about their nature. Negative values of  $\Delta k'_m$  are obtained when repulsion forces between molecules of the two different species of polymers are present, whereas positive values may be attributed to attractive force between the two components.

## MATERIALS AND METHODS

### Materials

Eudragit E 100 (EuE): poly[butyl methacrylate, (2-dimethylaminoethyl)methacrylate methyl methacrylate]; molar proportions of the monomer units 1 : 2 : 1; molecular weight 150,000 Da (Röhm, Darmstadt, Germany); Eudragit RL 100 (EuRL): poly(ethyl acrylate, methyl methacrylate, trimethylammonioethyl methacrylate chloride); molar proportions of the monomer units 1 : 2 : 0.2; molecular weight 150,000 Da (Röhm, Darmstadt, Germany); Eudragit RS 100 (EuRS): poly(ethyl acrylate, methyl methacrylate, trimethylammonioethyl methacrylate chloride); molar proportions of the monomer units 1 : 2 : 0.1; molecular weight 150,000 Da (Röhm, Darmstadt, Germany); Eudragit S 100 (EuS): poly(methacrylic acid, methyl methacrylate); molar

**Table II Values of Intrinsic Viscosity ( $[\eta]$ ), Huggins Constant ( $k'$ ), and Kraemer Constant ( $k''$ ) of EuRS in the Different Organic Solvents**

Solvent	$[\eta]$	$k'$	$k''$
Acetone	0.17	0.351	0.151
Methylene chloride	0.20	0.46	0.09
Ethyl acetate	0.12	1.86	-0.65
Ethanol	0.17	0.07	0.32
Isopropanol	0.15	0.14	0.28
Methanol	0.15	0.19	0.24
Tetrahydrofurane	0.15	1.60	-0.51

proportions of the monomer units 1 : 2; molecular weight 135,000 Da (Röhm, Darmstadt, Germany); Eudragit L 100 (EuL): poly(methacrylic acid, methyl methacrylate); molar proportions of the monomer units 1 : 1; molecular weight 135,000 Da (Röhm, Darmstadt, Germany); Eudragit NE 40 D (EuNE) poly(ethyl acrylate, methyl methacrylate); molar proportions of the monomer units 1 : 1; molecular weight 800,000 Da (Röhm, Darmstadt, Germany). This material is supplied as aqueous dispersion containing 40% w/w of the copolymer. To obtain the solid material, the dispersion was dried and washed with water until the presence of other additives was not detectable using UV-VIS spectra analysis. All polymers were kindly donated by Rofarma, Röhm, Italy. Analytical grade acetone, methylene chloride, ethyl acetate, ethanol, isopropanol, methanol, and tetrahydrofurane were used.

### Viscosity Measurements

The viscosity of the polymeric solutions was measured with an Ubbelohde viscometer 200 sec (Permax, MI, Italy). The measurements were performed at constant temperature of  $25 \pm 0.1^\circ\text{C}$  in a thermostated water bath (Haake F6, Karlsruhe, Germany). The  $k'$  and the  $k''$  of each copolymer were calculated by means of linear regression analysis from the plots of the  $\eta_{\text{red}}$  and  $\eta_{\text{in}}$  vs the concentration respectively according to eq. (7) and eq. (8). The average of the intercepts with the y axis of the two plots gives the intrinsic viscosity of the copolymer. The results were the mean of six determinations and the single experiment was accepted when the V.C. was less than 1%.

### Determination of the Good Solvent

The power of the solvent for the copolymers was determined on the basis of the Huggins constant

$k'$  value. A solvent was accepted as good when  $k'$  was approximately 0.30–0.35.

### Selection of the Solvent and Blending

The solvent for the programmed blends was chosen on the basis of the results concerning the determination of the good solvent. If the good solvent did not match for both copolymers, the more suitable one was chosen. The polymeric blends were prepared by mixing individual polymeric solutions. The compositions of the blends are given in Table I.

## RESULTS AND DISCUSSION

### Determination of the Good Solvent

For all the tested copolymers,  $k'$  was influenced to a greater extent than  $[\eta]$  by the solvent. As an example,  $[\eta]$ ,  $k'$ , and  $k''$  values of EuRS dissolved in each of the organic solvent studied are reported in Table II. Table III shows the best solvent and the more relevant calculated constants for each copolymer. Based on these preliminary studies, the selected solvent for the following compatibility studies were: 1. acetone for the series numbers 1–5 and number 10; and 2. THF for the series numbers 6–9.

### Compatibility Evaluation for Polymer-Polymer-Solvent Systems

The blends made of a cationic copolymer and an anionic copolymer (Table I, series numbers 4–7) showed the formation of visible aggregates. Furthermore, it is known that acid and basic methacrylic copolymers, when mixed in various ratios in a common solvent, form primary association complexes that are so stable that they do not dissociate

**Table III Values of Intrinsic Viscosity ( $[\eta]$ ), Huggins Constant ( $k'$ ), and Kraemer Constant ( $k''$ ) of the Different Polymers in the Selected Good Solvent**

Polymer	Solvent	$[\eta]$	$k'$	$k''$
EuRS	Acetone	0.173	0.351	0.151
EuRL	Acetone	0.181	0.393	0.130
EuE	Acetone	0.185	0.249	0.199
EuS	Tetrahydrofurane	0.41	0.37	0.14
EuL	Tetrahydrofurane	0.39	0.37	0.14
EuNE	Acetone	2.495	0.325	0.153



**Table IV** Values of  $[\eta]$ ,  $b_m$ , and  $k'_{m,\text{exp}}$  of the Different Blends

Series No.	Composition of the Blends		$[\eta]$	$b_m$	$k'_{m,\text{exp}}$
	Polymers	Weight Ratio			
1	EuE/EuRL	0.3:0.7	0.18	0.01	0.27
		0.5:0.5	0.18	0.03	0.28
		0.7:0.3	0.18	0.01	0.29
2	EuE/EuRS	0.3:0.7	0.18	0.01	0.27
		0.5:0.5	0.18	0.01	0.29
		0.7:0.3	0.18	0.01	0.29
3	EuE/EuNE	0.3:0.7	2.07	0.01	0.03
		0.5:0.5	1.59	0.03	0.01
		0.7:0.3	0.91	0.01	0.15
8	EuL/EuNE	0.3:0.7	2.27	0.01	0.09
		0.5:0.5	1.68	0.03	0.05
		0.7:0.3	1.29	0.01	0.18
9	EuL/EuS	0.3:0.7	0.44	0.01	0.20
		0.5:0.5	0.44	0.03	0.18
		0.7:0.3	0.25	0.01	0.05
10	EuRL/EuRS	0.3:0.7	0.18	0.01	0.27
		0.5:0.5	0.17	0.03	0.36
		0.7:0.3	0.19	0.01	0.22

upon dilution.<sup>1</sup> The same blends were prepared also by using all the other selected solvents; however, the behavior of the mixtures of the two copolymers was the same and consequently the viscosity measurements were not performed. The viscosity was determined for all the other mixtures in which phenomena of aggregation were not noticeable, and in Table IV the most relevant parameters are reported. The behavior of the different pairs of copolymers was evaluated according to the Theoretical Considerations section.

The  $\Delta b$  values were generally very small due to the fact that the copolymers are all methacrylic derivatives with similar molecular weight and  $b_{12}$  value is affected by  $[\eta]$  that depends on the molecular weight (Table V). However, the  $\Delta b$  values showed that the cationic copolymers EuRL and EuRS could be considered compatible with copolymer EuE. The neutral EuNE copolymer was incompatible with both EuL and EuE; in this case  $\Delta b$  values showed the most evident repulsive interactions (Table V). Finally, the copolymers EuL and EuS could be considered incompatible. In the case of EuRL/EuRS blends, the weight ratio seems to influence the behavior of the two polymers. On the basis of our data, the theory could be considered valid for the evaluation of compatibility of methacrylic copolymer blends.

The evaluation of the  $\Delta k'_m$  values (Table V) of the tested polymeric mixtures confirmed the re-

sults obtained with the  $\Delta b$  analysis. The differences between the  $k'_{m,\text{exp}}$  and  $k'_{m,\text{cal}}$  were, generally, bigger than  $\Delta b$ , suggesting a higher robustness of the  $\Delta k'_m$  analysis. Moreover, the  $\Delta k'$

**Table V** Values of  $\Delta b$  and  $\Delta k'_m$  of the Different Blends

Series No.	Composition of the Blends		$\Delta b$	$\Delta k'_m$
	Polymers	Weight Ratio		
1	EuE/EuRL	0.3:0.7	0.005	0.121
		0.5:0.5	0.005	0.163
		0.7:0.3	0.007	0.179
2	EuE/EuRS	0.3:0.7	0.003	0.072
		0.5:0.5	0.002	0.120
		0.7:0.3	0.001	0.119
3	EuE/EuNE	0.3:0.7	-2.165	-0.285
		0.5:0.5	-1.024	-0.282
		0.7:0.3	-2.144	-0.115
8	EuL/EuNE	0.3:0.7	-0.276	-0.340
		0.5:0.5	-0.167	-0.330
		0.7:0.3	-0.178	-0.130
9	EuL/EuS	0.3:0.7	-0.027	-0.043
		0.5:0.5	-0.027	-0.038
		0.7:0.3	-0.031	-0.188
10	EuRL/EuRS	0.3:0.7	-0.002	0.029
		0.5:0.5	0.004	0.181
		0.7:0.3	-0.005	0.070

analysis of the series number 10 (EuRL/EuRS blends) allowed to establish that the two polymers were always compatible and the maximum value was obtained for the 0.5 : 0.5 weight ratio composition. Only for this series, the  $\Delta b$  and  $\Delta k'$  results are incoherent, as the  $\Delta b$  values are very small they can be affected both by experimental errors and/or mathematical analysis.

## CONCLUSION

According to the mathematical models reported in the Theoretical Considerations section, the tested polymeric systems were not ideal because consistent hydrodynamic interactions were not negligible and the viscosity measurements could provide a measure of the nature of the interpolymeric interactions. Moreover, the study of  $\Delta k'$  was more robust than  $\Delta b$  analysis in the evaluation of the interactions of the different pairs of methacrylic copolymers.

The compatibility of different pairs of methacrylic copolymers with similar molecular weights and structures can be evaluated by using capillary viscometry and, consequently, this type of analysis can be useful in pharmaceutical preformulation studies.

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