

# Interpolymer specific interaction in blends of poly(styrene-*co*-alkyl acrylate-*co*-4-vinylpyridine) and poly(styrene-*co*-alkyl acrylate-*co*-acrylic acid)

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## Abstract

The interpolymer specific interaction of proton donating polymer (PDP) and proton accepting polymer (PAP) in toluene was studied by viscometry coupled with light scattering. The viscometric experiment results show that the stronger the interpolymer interaction is, the higher the viscosity of PDP/PAP blend solution than the weight-average of both components at high concentration, in contrast to lower viscosity at low concentration. Based on the relationship of viscosity enhancement factor with polymer level in solution, a new polymer–polymer interaction parameter  $k_a$  to estimate interpolymer interaction was developed. The effects of functional groups content and acrylate unit on interpolymer interaction were studied with this parameter combined with light scattering. The results show that interpolymer interaction ability increases with the functional group and long chain alkyl acrylate content. With the increase in side chain length of acrylate unit, enhancement in the interpolymer specific interaction can be realized. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Specific interaction; Light scattering; Viscometry

## 1. Introduction

Interpolymer specific interaction has attracted extensive attention because polymer complexes via specific interaction have unusual properties that are dramatically different from non-complexed parent polymers. Interpolymer complexes can be formed by intermolecular secondary binding forces due to the incorporation of a relatively few associating functional groups into the polymer chains. Inter-macromolecular secondary binding forces include ion–ion Coulombic interaction, hydrogen bonding and transition metal complexation, etc. [1].

In low-polarity solvents polymer complexes exhibit strong intermolecular association leading generally to the variation of solution viscosity and accordingly to unique solution properties that have various potential applications such as flow improvers and viscosity modifiers for oil transport [2]. Viscometric technique therefore has proved and widely used as a simple and effective method monitoring intermolecular association and complexation.

Generally, there are some viscometric methods employed to study interpolymer specific interaction. One method consists in the effect of intermolecular association on solution viscosity. For example, Weiss and Lu [3] studied the solution viscosities of blends of lighted sulfonated polystyrene (SPS) and poly(styrene-*co*-4-vinylpyridine) (PSVP) in DMF with the viscosity enhancement factor,  $R$ . PSVP and SPS were blended resulting in higher solution viscosities than comparable blends assumed without complexation. Pan et al. [4,5], using the same method as Weiss did, reported the improved solution viscosities for blends of carboxylated poly(phenyl oxide) (CPPO) and PSVP in  $\text{CHCl}_3/\text{CH}_3\text{OH}$  ( $v/v = 96:4$ ) where the interaction occurred between carboxyl and vinylpyridine attached to CPPO and PSVP chains, respectively. Contrary to what Weiss and Pan described, however, Jiang et al. [6] found the viscosity of the complexed solution formed by poly(styrene-*co*-vinylphenol) (PSTVPh) and PSVP decreased in THF since interpolymer complexation via hydrogen bonding in solution accompanies contraction or collapse of the component polymer coils. Therefore, the method of viscosity enhancement factor, we think, is generally empirical depending on functional unit density and solvent used, etc. Other methods are based on such viscometric parameters as Huggins coefficient and intrinsic viscosity. Intrinsic viscosity data

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for ternary system comprising polymer1–polymer2–solvent have been employed to study the interaction between unlike polymers by García and Abdel-Azim [7–9]. But the intrinsic viscosity of the polymer blend is affected by such influencing factors as molecular weight, the structure and shape of the blends as well as solvent properties. Either positive or negative deviation of intrinsic viscosity of the polymer blend from the additivity law of the component intrinsic viscosities was reported in the literatures. Theoretical considerations based on Huggins equation, such as  $\Delta b$  criterion and  $\alpha$  criterion, were thus developed to estimate the interpolymer interaction [7–19]. But the corresponding variation in intrinsic viscosity has not been taken into account in these methods because these methods are based on a theoretical premise that there is no deviation of the experimental intrinsic viscosity of the blend,  $[\eta]_{m,exp}$ , from the theoretical intrinsic viscosity of the blend,  $[\eta]_{m,cal}$ . In our experiments, in addition to the deviation of  $[\eta]_{m,exp}$  from  $[\eta]_{m,cal}$ , the dependence of reduced viscosity  $\eta_{sp}/C$  on polymer concentration  $C$  are curved even in dilute region. Under such circumstances, Huggins equation cannot be used as a basis for a general procedure depicting the polymer solution behavior. Therefore, a novel interpolymer interaction parameter  $k_a$  was proposed to estimate the interpolymer specific interaction in this work.

Until now, there are few reports on interpolymer specific interaction between long chain alkyl acrylate copolymers containing functional groups. In the present paper, poly(styrene-*co*-alkyl acrylate-*co*-acrylic acid) and poly(styrene-*co*-alkyl acrylate-*co*-4-vinylpyridine) were used as proton donating polymer (PDP) and proton accepting polymer (PAP), respectively. The effects of functional groups content and macromolecular chain composition on interpolymer interaction were investigated through  $k_a$  and static light scattering (SLS).

## 2. Theoretical consideration

### 2.1. Viscosity enhancement factor

Polymer–polymer specific interactions in solution always result in the change in blend solution viscosity compared to that without specific interaction, depending on interaction strength and solution concentration. The additivity law of component viscosities has been conveniently used as a criterion for determining the formation of interpolymer complex. In the case of polymer blend without interpolymer specific interaction, a linear dependence of viscosities of the blend of two polymers on its composition is observed. The specific viscosity of the blend,  $\eta_{sp,m,cal}$ , can be calculated as a weight-average of the specific viscosities of both components [3], as given by Eq. (1)

$$\eta_{sp,m,cal} = (\eta_{sp,1}C_1 + \eta_{sp,2}C_2)/C_m \quad (1)$$

where  $\eta_{sp,1}$  and  $\eta_{sp,2}$  are the specific viscosities of

components 1 and 2 at concentration  $C_m = C_1 + C_2$ , respectively. When there are specific interactions in the blend, the solution viscosity of the blend will generally be different from the value given by Eq. (1). Thus, as suggested by Weiss, a viscosity enhancement factor,  $R$ , can be defined as

$$R = (\eta_{sp,m,exp} - \eta_{sp,m,cal})/\eta_{sp,m,cal} \quad (2)$$

where  $\eta_{sp,m,exp}$  and  $\eta_{sp,m,cal}$  are the experimental and theoretical specific viscosities of the blend solution, respectively; the latter given by Eq. (1).

### 2.2. Evaluation of interaction for ternary system based on viscometric parameters

In this study, the dependence of reduced viscosity  $\eta_{sp}/C$  on the concentration  $C$  are curved for polymer blends as well as the component polymers. The relationship between  $\eta_{sp}/C$  and  $C$  may be given by Schulz–Blaschke equation, as shown in Eq. (3), to describe the polymer solution behavior

$$\eta_{sp}/C = [\eta] + k_{SB}[\eta]\eta_{sp} = \frac{[\eta]}{1 - k_{SB}[\eta]C} \quad (3)$$

where  $[\eta]$  is intrinsic viscosity and  $k_{SB}$  the Schulz–Blaschke coefficient. For a solution of two unlike polymers without interpolymer specific interactions between them, similar to Eq. (1), the specific viscosity can be calculated as a weight-average of the specific viscosities of both components, given by Eq. (4) in terms of Schulz–Blaschke equation

$$\begin{aligned} \eta_{sp,m,cal} &= \frac{[\eta]_1 w_1 C_m}{1 - k_1 [\eta]_1 C_m} + \frac{[\eta]_2 w_2 C_m}{1 - k_2 [\eta]_2 C_m} \\ &\approx \frac{[\eta]_{m,cal} C_m}{1 - k_{m,cal} [\eta]_{m,cal} C_m} \end{aligned} \quad (4)$$

where  $w_1$  and  $w_2$  are weight fractions of component 1 and 2 in the polymer blend, respectively.  $k_1$  and  $k_2$  are Schulz–Blaschke coefficients.  $C_m$  is the sum of concentrations of both components.  $k_{m,cal}$  is the theoretical Schulz–Blaschke coefficient of the polymer blend and approximates to an average calculated by Eq. (5) within a tolerance of errors over the range of measured concentration

$$k_{m,cal} = \frac{k_1 [\eta]_1^2 w_1 + k_2 [\eta]_2^2 w_2}{([\eta]_1 w_1 + [\eta]_2 w_2)^2} \quad (5)$$

If the relationship between the reduced viscosity and concentration follow Schulz–Blaschke equation for both components and complexed blend system, it can be deduced that viscosity enhancement factor,  $R$ , is related to the theoretical specific viscosity of the blend solution,  $\eta_{sp,m,cal}$ , by an expression as follows:

$$\frac{1}{R + 1} = \frac{[\eta]_{m,cal}}{[\eta]_{m,exp}} - k_a \eta_{sp,m,cal} \quad (6)$$

$k_a$  is related to theoretical and experimental Schulz–Blaschke coefficient and intrinsic viscosity by:

$$k_a = k_{m,exp} - k_{m,cal} \frac{[\eta]_{m,cal}}{[\eta]_{m,exp}} \quad (7)$$

The product  $k_a \eta_{sp,m,cal}$  expresses the extent of interpolymer interaction and  $k_a$  value can therefore be considered as a contribution expressing the interpolymer interaction ability in a given complexed system.

### 3. Experimental

#### 3.1. Polymers

A series of PDP and PAP was prepared by radical emulsion copolymerization at 60 °C under nitrogen with potassium persulfate as the initiator and sodium lauryl sulfate as the emulsifier. The copolymers from the emulsion were isolated by precipitation in cold methanol and then further purified by repeating the process of redissolution in toluene and reprecipitation in methanol.

The molecular weights of PDP were examined by size exclusion chromatography (elution with THF at 30 °C on cross-linked polystyrene; rate 1 ml/min, calibration with polystyrene standards) and SLS, respectively. The molecular weights of PAP and the molar masses of the complexes formed by PDP and PAP were determined by SLS. The carboxyl content in PDP was determined by titration of PDP in toluene/methanol (4/1, v/v) solution to a phenolphthalein end point with a solution of sodium hydroxide in methanol. The VP content in PAP was determined by titration with a perchloric acid solution in glacial acetic acid. The contents of styrene unit and alkyl acrylate unit in copolymers were calculated from JEOL FX 90Q <sup>1</sup>H NMR analysis in CDCl<sub>3</sub> at 30 °C (chemical shift of  $\delta$  6.8–7.2 ppm is attributed to hydrogen atom in phenyl; and chemical shift of  $\delta$  0.8–1.0 ppm is attributed to three hydrogen atoms of CH<sub>3</sub> in alkyl acrylate unit). The comonomer compositions are listed in Table 1.

#### 3.2. Viscosity measurements

The individual polymer solutions were prepared by dissolving the polymers in toluene. Complexed solutions of PDP with PAP were prepared by blending two corresponding polymer solutions in the appropriate proportions in toluene. The reduced viscosities of the polymers and their blend solutions were measured by a Ubbelohde viscometer at 30 °C with an accuracy of 0.05 °C. The viscometer was calibrated using several standard solvents. The data were evaluated according to Schulz–Blaschke equation. The intrinsic viscosities and Schulz–Blaschke coefficients of component polymers are listed in Table 1.

#### 3.3. Static light scattering

Light scattering measurements were performed on a Dawn photometer using polarized light of wavelength 632.8 nm from a He–Ne laser (Wyatt Co.). The Optilab DSP differential refractometer was operated at the same condition of light scattering measurement for obtaining

the refractive index increment values,  $dn/dc$ , of polymers in toluene. The  $dn/dc$  values for each component polymer at 30 °C in toluene are listed in Table 1. The intensity of scattered light was detected at angles ranging from 26 to 142°. Toluene was purified by distillation and filtered through 0.02  $\mu$ m Whatman pore size nylon filters prior to use. The solutions of the component polymers and their blend solution were clarified by filtration through 0.5  $\mu$ m pore size nylon filters.

Static light scattering data were evaluated by Berry method for the polymers with high molecular weight

$$\sqrt{\frac{KC}{R(\theta)}} = \frac{1}{\sqrt{M_w P(\theta)}} + A_2 C \sqrt{MP(\theta)} \quad (8)$$

where  $K$  is an optical constant including  $dn/dc$ ,  $C$  the polymer solution concentration,  $R(\theta)$  the difference between the Rayleigh ratio of the solution and that of the pure solvent,  $M_w$  the weight-average molecular weight,  $A_2$  the second virial coefficient,  $P(\theta)$  the particle scattering function in terms of  $1 + q^2 R_g^2/3$ , where  $q = (4\pi n/\lambda_0)\sin(\theta/2)$  is the magnitude of the scattering vector.

Weight-average molecular weight of PDP and PAP,  $M_D$  and  $M_A$ , given in Table 1, and molar mass of their complex,  $M_a$ , ( $dn/dc$  of complexed solution was calculated by using the additive rule of both component polymers) were obtained from the double extrapolation of  $[KC/R(\theta)]^{1/2}$  at zero angle and zero concentration by means of least square method.

### 4. Results and discussion

Prior to the discussion of data on polymer blend, it is necessary to characterize the viscometric behaviors of component polymers as well as complexed systems in toluene. Measurements of the reduced viscosities of the solutions have been conducted and their respective plots were fitted through Schulz–Blaschke equation. The values of  $[\eta]$  and Schulz–Blaschke coefficient were determined by linear regression analysis of the plots of  $C/\eta_{sp}$  versus  $C$ . The Table 2 lists the theoretical and experimental Schulz–Blaschke coefficients and intrinsic viscosities for the complexed systems studied in this paper. The  $\gamma$  values are correction factors in linear regression analysis and almost equal to unity, showing the experimental data follow well the typical linear relationship of the Schulz–Blaschke equation.

#### 4.1. Effect of polymer level on solution behavior

Weiss et al. and Pan et al. estimated the interpolymer interaction ability according to  $R$  at the same solution concentration. But this method, available to the system formed by both components with similar viscosities, is improper to those systems in which viscosities of both components at the same concentration were sufficiently apart. In view of definition of  $R$ , compared to solution concentration as a scale when comparing interpolymer specific interaction between different complexed systems

Table 1  
Characteristics of component polymers

Component <sup>a</sup>	AA (%)	VP (%)	St (%)	Acrylate (%)	$[\eta]$ (dl/g)	$k_{SB}$	$M_{SEC,w} \times 10^{-4b}$	$M_{w,LLS} \times 10^{-4}$	$dn/dc$
D2.2 – 50LA	2.2	–	47.8	50.0	3.253	0.335	106	469	0.060
D2.2 – 50OA(I)	2.2	–	44.0	53.8	3.083	0.362	96	424	0.050
D2.1 – 50OA(II)	2.1	–	42.5	55.4	2.108	0.232	78	390	0.050
D1.2 – 50OA	1.2	–	46.5	52.3	3.914	0.404	115	356	0.038
D2.1 – 15OA	2.1	–	82.7	15.2	2.478	0.399	77	191	0.081
D2.2 – 50BA	2.2	–	43.8	54.0	3.027	0.329	108	349	0.037
A6.1 – St	–	6.1	93.9	–	5.699	0.336	–	320	0.11
A5.6 – 50LA	–	5.6	49.4	45.0	2.766	0.323	–	269	0.048
A9.2 – 50OA	–	9.2	38.8	52.0	3.587	0.407	–	273	0.040
A5.7 – 50OA	–	5.7	47.0	47.3	4.670	0.341	–	406	0.046
A3.7 – 50OA	–	3.7	41.7	54.6	5.122	0.393	–	497	0.043
A5.3 – 15OA	–	5.3	78.5	16.2	4.907	0.353	–	395	0.093
A5.5 – 50BA	–	5.5	38.7	55.8	4.582	0.444	–	395	0.045

<sup>a</sup> Dx – y and Ax – y represent PDP and PAP, respectively, x is the functional monomer content in wt% and y denotes the approximate alkyl acrylate monomer content in wt%; BA, OA, and LA denote butyl acrylate, octyl acrylate, and lauryl acrylate, respectively.

<sup>b</sup> Weight-average molecular weights of PDP are determined by SEC in view of taking into account carboxyl association with PDP in toluene resulting in  $M_{w,LLS}$  much overestimated as shown in  $M_{w,LLS}$  column.

according to  $R$ , it seems more reasonable that theoretical specific viscosity of the blend solution  $\eta_{sp,m,cal}$ , related to the hydrodynamic volume fraction of solute by Einstein equation, is used as a scale for polymer level in solution.

Here, particular attention was first paid to the effect of polymer level in solutions on interpolymer specific interaction. Fig. 1 shows  $R$  as a function of  $\eta_{sp,m,cal}$  for D2.2 – 50OA(I)/A5.7 – 50OA blends in toluene with different weight ratio of D2.2 – 50OA(I) to A5.7 – 50OA. As anticipated,  $R$  generally increases with  $\eta_{sp,m,cal}$  in the entire experimental range. The higher the polymer level in solution originating from the increase in concentration is, the more is the functional groups per unit volume and total carboxyl–vinylpyridine interaction in the blend thus increases. But for some D2.2 – 50OA(I)/A5.7 – 50OA systems, the  $R$  will show negative values in very dilute region. It can be verified from Table 2 by the fact that the experimental intrinsic viscosities of the blend solutions,  $[\eta]_{m,exp}$ , are compared with their weighted average values,  $[\eta]_{m,cal}$  ( $[\eta]_{m,cal} = [\eta]_1 w_1 + [\eta]_2 w_2$ , where  $w_1$  and  $w_2$  are weight fraction of PDP and PAP in the blend, respec-

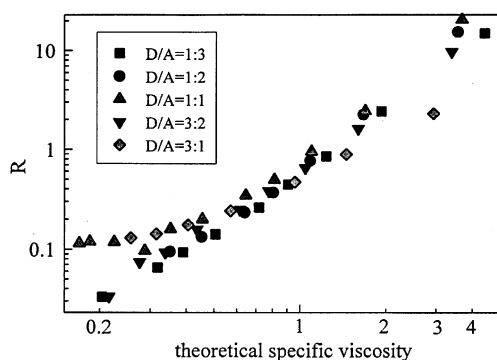


Fig. 1.  $R$  as a function of  $\eta_{sp,m,cal}$  for D2.2 – 50OA(I)/A5.7 – 50OA blends in toluene with different weight ratios of PDP/PAP.

tively), and found to be slightly lower than  $[\eta]_{m,cal}$  for some D2.2 – 50OA(I)/A5.7 – 50OA systems as well as other complexed systems. That is to say  $R$  may be negative at zero concentration. With the increase in  $\eta_{sp,m,cal}$  of the blend solution, the  $R$  exhibiting negative value in very dilute region becomes larger and changes to a positive value. Obviously,  $R$  shows positive or negative value depending on polymer levels in solution as well as interaction strength. In very dilute region, the blend molecules are contracted by strong acid–base interaction of functional groups with the formation of a compact structure, which reduces the viscosity of the complexed solution, i.e.  $R < 0$ . The solution behavior in very dilute region is similar to results described by Jiang et al. for blends of PSTVPh/PSVP with considerable functional units, where insoluble complexes were formed when the blend solution concentrations increased. With respect to the present systems having small amount of functional groups, when the blend solution concentration increases, the isolated associates combine and lead to the formation of an intermolecular complex structure. This leads to a higher viscosity.

It cannot be considered as an indication of  $R = 0$  that there is no interpolymer specific interaction, i.e.  $R$  might be zero even in the blend solution with interpolymer specific interaction. Therefore, it is more appropriate that an extent to which  $R$  increases with  $\eta_{sp,m,cal}$  is used to act as a measure of the interpolymer interaction ability than  $R$  itself. The parameter  $k_a$  in Eq. (7), reflecting the extent of the increase in  $R$  with  $\eta_{sp,m,cal}$ , will be used to study the interpolymer specific interaction ability in Section 4.2.

#### 4.2. Effect of functional group content on specific interaction

The dependence of  $k_a$  on the functional group content is shown in Fig. 2(A) and (B) which shows the values of  $k_a$  for

Table 2  
Viscometric data for PDP/PAP systems

Polymer blend	$F_{AA}$	$k_{m,exp}$	$k_{m,cal}$	$[\eta]_{m,cal}$	$[\eta]_{m,exp}$	$k_a$	$\Delta[\eta]_m/[\eta]_{m,cal}$ <sup>a</sup>	$\gamma$
D2.2 – 50LA/A5.6 – 550LA	0.222	0.800	0.330	2.928	2.747	0.448	–0.062	0.9975
	0.276	0.927	0.331	2.961	2.672	0.560	–0.098	0.9991
	0.394	0.840	0.332	3.025	2.795	0.480	–0.076	0.9996
	0.533	0.789	0.334	3.090	2.857	0.428	–0.076	0.9992
	0.632	0.691	0.334	3.131	3.014	0.344	–0.037	0.9992
D2.2 – 50OA(I)/A9.2 – 50OA	0.209	0.809	0.405	3.371	3.552	0.425	0.054	0.9995
	0.261	1.072	0.404	3.335	3.018	0.626	–0.095	0.9995
	0.346	1.043	0.401	3.285	3.021	0.607	–0.080	1.0000
	0.413	0.911	0.400	3.251	3.102	0.492	–0.046	0.9999
	0.514	0.837	0.397	3.209	3.181	0.436	–0.009	0.9999
D2.2 – 50OA(I)/A5.7 – 50OA	0.158	0.79	0.381	4.185	4.006	0.392	–0.043	0.9999
	0.219	0.926	0.384	4.063	3.624	0.496	–0.108	0.9981
	0.360	0.839	0.389	3.818	3.745	0.443	–0.019	0.9968
	0.458	0.836	0.391	3.671	3.496	0.425	–0.048	0.9994
	0.628	0.687	0.392	3.450	3.551	0.306	0.029	0.9999
D2.2 – 50OA(I)/A3.7 – 50OA	0.220	0.713	0.403	4.630	4.726	0.318	0.021	0.9991
	0.297	0.779	0.405	4.466	4.477	0.375	0.002	0.9995
	0.458	0.701	0.406	4.137	4.323	0.312	0.045	0.9964
	0.657	0.661	0.401	3.754	4.048	0.289	0.078	0.9996
D2.2 – 50OA(I)/A6.1 – St	0.149	0.658	0.355	5.062	4.449	0.254	–0.121	0.9991
	0.208	0.687	0.361	4.850	4.219	0.272	–0.130	0.9999
	0.345	0.727	0.372	4.426	3.937	0.308	–0.110	0.9996
	0.513	0.689	0.380	4.001	3.755	0.284	–0.061	0.9998
	0.612	0.641	0.382	3.789	3.684	0.248	–0.028	0.9996
D1.2 – 50OA/A5.7 – 50OA	0.170	0.677	0.359	4.637	4.510	0.308	–0.027	0.9991
	0.218	0.781	0.364	4.545	4.295	0.396	–0.055	0.9998
	0.358	0.817	0.376	4.342	4.202	0.428	–0.032	0.9988
	0.528	0.714	0.387	4.174	4.186	0.328	0.003	0.9992
D2.1 – 150A/A5.7 – 50OA	0.212	0.658	0.398	4.110	3.949	0.244	–0.039	0.9999
	0.350	0.839	0.413	3.700	3.458	0.397	–0.065	0.9990
	0.517	0.824	0.425	3.292	3.146	0.380	–0.044	0.9997
	0.634	0.784	0.427	3.053	2.934	0.339	–0.039	0.9994
	0.682	0.623	0.427	2.962	2.968	0.197	0.002	0.9865
D2.1 – 150A/A5.3 – 150A	0.278	0.611	0.394	3.933	3.794	0.203	–0.035	0.9979
	0.366	0.750	0.403	3.694	3.475	0.321	–0.059	0.9991
	0.535	0.683	0.416	3.291	3.270	0.264	–0.006	0.9994
	0.698	0.594	0.420	2.966	3.094	0.191	0.043	0.9988
D2.2 – 50BA/A5.5 – 50BA	0.163	0.659	0.440	4.193	3.891	0.184	–0.072	0.9997
	0.226	0.745	0.437	4.064	3.650	0.258	–0.102	0.9985
	0.368	0.711	0.426	3.805	3.472	0.244	–0.087	0.9933
	0.538	0.656	0.407	3.546	3.285	0.216	–0.074	0.9968
	0.636	0.536	0.394	3.416	3.529	0.155	0.033	0.9972

<sup>a</sup>  $\Delta[\eta]_m = [\eta]_{m,exp} - [\eta]_{m,cal}$ .

D2.2 – 50OA(I)/A<sub>x</sub> – 50OA ( $x = 9.2, 5.7,$  and  $3.7$ ) and D<sub>x</sub> – 50OA/A5.7 – 50OA ( $x = 1.2$  and  $2$ ) as a function of  $F_{AA}$  ( $F_{AA}$  refers to molar fraction of AA groups calculated by dividing the molar number of carboxyl by the total molar number of VP and carboxyl in the blend) in toluene. Here, when the functional group content of one component is fixed, the values of  $k_a$  are generally increased with the functional group content of another component, i.e. the interpolymer interaction ability is increased with functional group level. The higher the functional group content in solution is, the

more is the functional groups per unit volume and total carboxyl–vinylpyridine interaction in the blend thus increases.

#### 4.3. Effect of composition of polymer components on interpolymer interaction

The results of  $k_a$  as a function of  $F_{AA}$  in the blends of D2.2 – 50OA(I) and two types of PAP with different OA content in toluene are shown in Fig. 3(A). It is obvious that

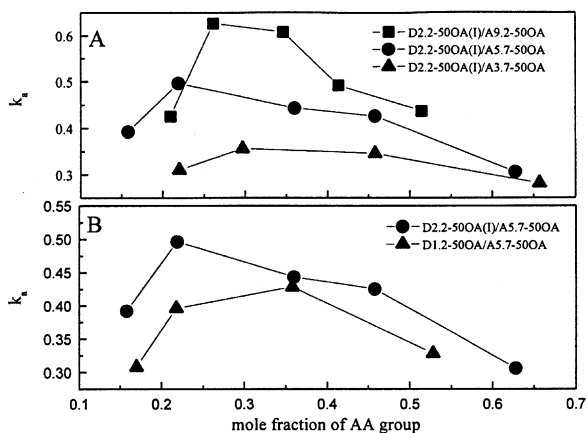


Fig. 2.  $k_a$  as a function of  $F_{AA}$  for (A) D2.2 – 50OA(I)/Ax – 50OA ( $x=9.2, 5.3$  and  $3.7$ ), (B) Dx – 50OA/A5.7 – 50OA ( $x=1.2$  and  $2$ ) in toluene.

$k_a$  increases with the content of OA in PAP. The effect of OA content on interpolymer interaction was further studied by changing OA content in PDP, as shown in Fig. 3(B) that shows  $k_a$  against  $F_{AA}$  for D2.1 – 15OA/A5.7 – 50OA and D2.1 – 15OA/A5.3 – 15OA in toluene. As it is similar to the result from Fig. 3(A), the interpolymer interaction ability increases with the OA content in component polymers according to the values of  $k_a$ . As regards the effect of different acrylates on interaction, it was studied by changing acrylate in component copolymers. The values of  $k_a$  for PDP/PAP blends with different acrylate constituent are shown in Fig. 4.

It is obtained from Fig. 4 that the interpolymer specific interaction ability is generally increased in turn of D2.2 – 50BA/A5.5 – 50BA, D2.2 – 50OA(I)/A5.7 – 50OA and D2.2 – 50LA/A5.6 – 50LA according to  $k_a$ . The interpolymer specific interaction ability for the latter two is

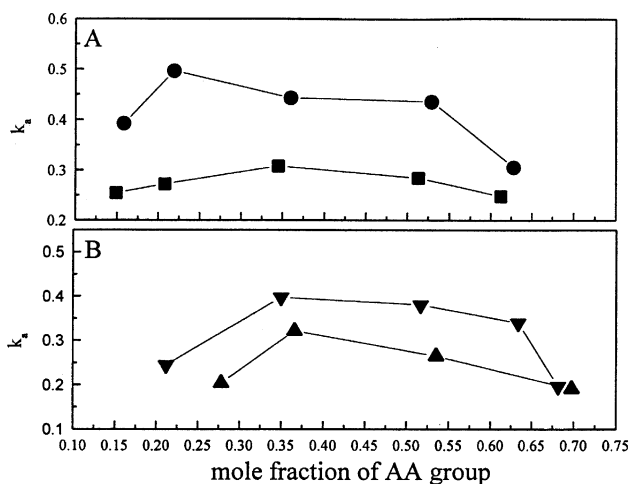


Fig. 3.  $k_a$  as a function of  $F_{AA}$  for polymer blend in toluene. (A) D2.2 – 50OA(I)/A5.7 – 50OA (●) and D2.2 – 50OA(I)/A6.1 – St (■), (B) D2.1 – 15OA/A5.7 – 50OA (▼) and D2.1 – 15OA/A5.3 – 15OA (▲).

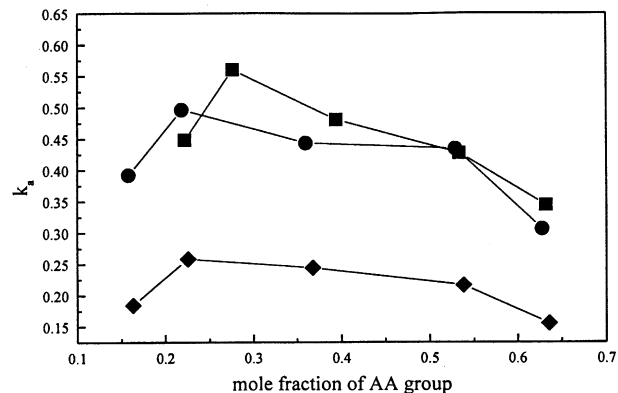


Fig. 4.  $k_a$  as a function of  $F_{AA}$  for D2.2 – 50LA/A5.6 – 50LA (■), D2.2 – 50OA(I)/A5.7 – 50OA (●), and D2.2 – 50BA/A5.5 – 50BA (◆) in toluene.

much stronger than the former. The result, together with what from Fig. 3, provides an indication of long chain alkyl acrylate playing an important role in interpolymer interaction between PDP and PAP. Malik et al. [20] suggested hydrogen bond formation between randomly distributed VP and AA groups in the complementary chains in the presence of bulky long chain alkyl acrylate cannot be visualized without considering the overlapping (van der Waals force) between side chains of long chain alkyl acrylate on two types of chains. But hydrogen bond formation between VP and AA groups on the complementary chains in the absence of bulky long chain alkyl acrylate can also be visualized in our experiment although the interaction strength is not as strong as in the presence of bulky long chain alkyl acrylate. When the side chains of long chain alkyl acrylate reach C<sub>8</sub>, the overlapping between side chains of alkyl acrylate becomes remarkable, therefore, we think the presence of bulky acrylate group makes it realized to form a larger and more stable gel-like structure of interpolymer complex.

#### 4.4. Interpolymer complexation in solution studied by SLS

Interpolymer complexation or association should accompany a variation of the particle size and molar mass. Therefore, LS is believed to be effective to monitor the variation. In this paper, attention is paid on the effect of functional group level and bulky long chain alkyl acrylate on interpolymer complexation from SLS.

Fig. 5(A) shows the square reciprocal reduced scattered intensity at zero angle,  $(KC/R_0)^{1/2}$ , against polymer concentration for D2.1 – 50OA(II)/A9.2 – 50OA, D2.1 – 50OA(II)/A5.7 – 50OA, and D2.1 – 50OA(II)/A3.7 – 50OA with  $F_{AA}$  of ca. 0.35 in toluene. Here we use D2.1 – 50OA(II) rather than D2.2 – 50OA(I) because the gyration radius of D2.2 – 50OA(I)/A9.2 – 50OA complex in dilute region exceeds over the filter membrane pore size ( $\phi$  0.5  $\mu$ m). It can be seen from Fig. 5(A) that when VP content is increased, molar masses of the complexes increase although the molecular weights of Ax – 50OA

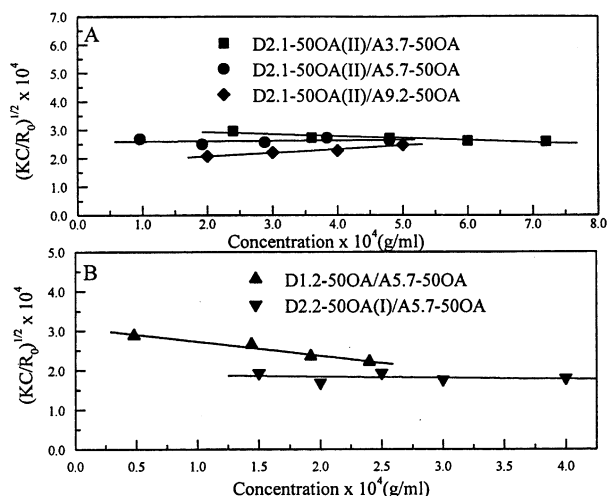


Fig. 5. The square reciprocal reduced scattered intensity at zero angle against polymer concentration for (A) D2.1 – 50OA(II)/Ax – 50OA ( $x = 9.2, 5.7$  and  $3.7$ ) with  $F_{AA}$  of  $0.35$  and (B) Dx – 50OA/A5.7 – 50OA ( $x = 1.2$  and  $2$ ) with  $F_{AA}$  of  $0.36$  in toluene.

are decreased. Likewise, when the AA content in PDP is increased, molar masses of the complexes increase accordingly, as shown in Fig. 5(B) which exhibits  $(KC/R_0)^{1/2}$  against polymer concentration for D1.2 – 50OA/A5.7 – 50OA and D2.2 – 50OA(I)/A5.7 – 50OA with  $F_{AA}$  of  $0.36$  in toluene. As it is the same as that obtained from viscometry, SLS experiments confirm that the higher the functional groups content, the stronger the interpolymer specific interaction.

The molar masses of the complexed systems with different  $F_{AA}$  were measured by SLS and a typical Berry plot for D2.2 – 50LA/A5.6 – 50LA with a  $F_{AA}$  of ca.  $0.394$  is given in Fig. 6. The impact of the content of octyl acrylate units in component polymers on interpolymer interaction is shown in Fig. 7(A) and (B), which shows the  $F_{AA}$  dependence of

the molar masses of polymer complexes on different OA compositions in toluene. The position of  $F_{AA} = 0$  and  $1$  correspond to individual PAP and PDP, respectively. van der Waals forces between side chains of octyl acrylate units on two types of chains are responsible for D2.2 – 50OA(I)/A5.7 – 50OA with the strongest complexation compared to other three complexed systems. Fig. 7(C) shows the dependence of the molar masses of the complexes on acrylate constituent for D2.2 – 50BA/A5.5 – 50BA, D2.2 – 50OA(I)/A5.7 – 50OA, and D2.2 – 50LA/A5.6 – 50LA. As is similar to that obtained from viscometric method, the result that molar mass of the complex increases with the length of side chain of acrylate unit can also be obviously attributed to more overlapping between side chains of acrylate on two types of chains, i.e. long chain alkyl acrylate unit makes positive contribution to interpolymer specific interaction between PDP and PAP. In addition, the molar mass plots show the similar variation trends to  $k_a$  for the systems studied in the present study although at some points there are small difference due to the different experimental concentration range for the two methods. As a rule,  $k_a$  parameter can act qualitatively as a measure of the magnitude of the interpolymer interaction ability.

## 5. Conclusion

Interpolymer interactions between long chain alkyl acrylate copolymers bearing proton donor and proton acceptor, respectively, were studied with viscometry and light scattering in toluene. It is suggested that the stronger the interpolymer interaction, the higher the  $R$  at high concentration compared with the lower  $R$  in very dilute region. The increase in interaction parameter  $k_a$  is the result of increasing interpolymer specific interaction ability. The combination of viscometry and light scattering shows that

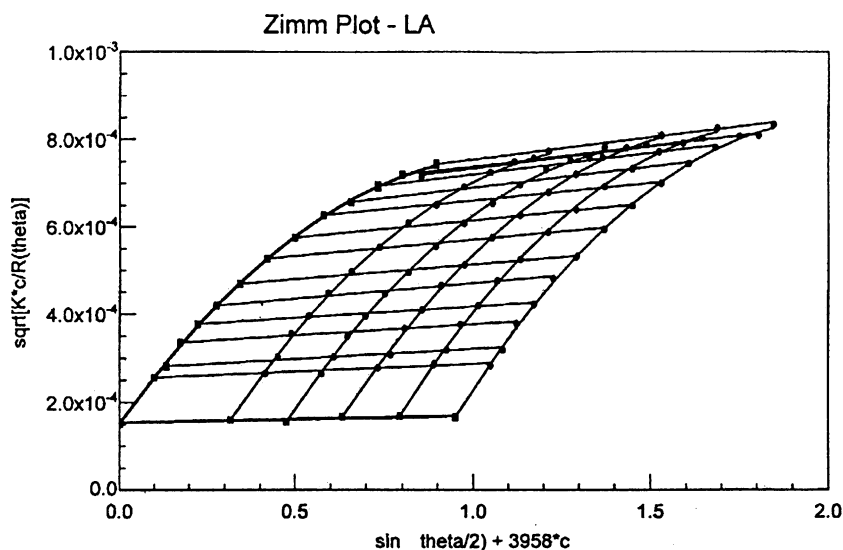


Fig. 6. The typical Berry plots of D2.2 – 50LA/A5.6 – 50LA with  $F_{AA}$  of  $0.394$ , concentration  $\times 10^4$  (g/ml):  $0.8, 1.2, 1.6, 2.0$ , and  $2.4$ .

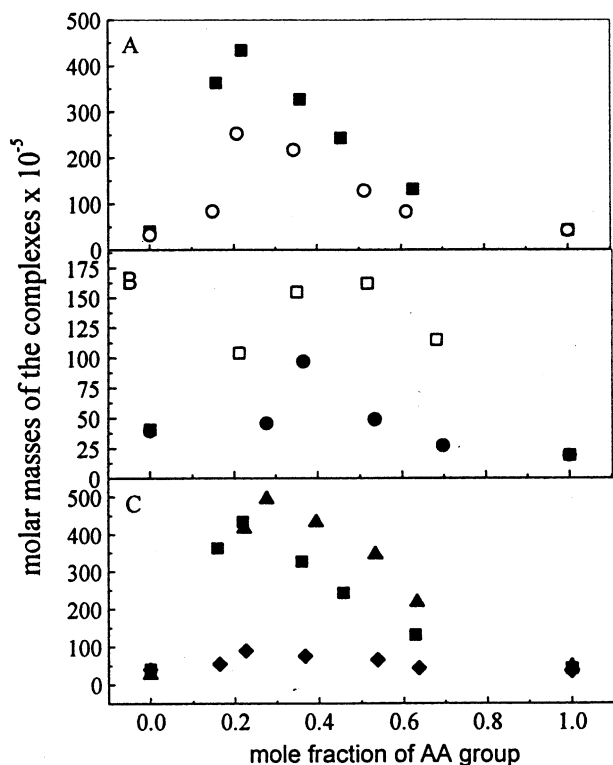


Fig. 7. The molar mass as a function of  $F_{AA}$  for complexed systems in toluene. (A) D2.2 – 50OA(I)/A5.7 – 50OA (■) and D2.2 – 50OA(I)/A6.1 – St (○), (B) D2.1 – 15OA/A5.7 – 50OA (□) and D2.1 – 15OA/A5.3 – 15OA (●), (C) D2.2 – 50LA/A5.6 – 50LA (▲), D2.2 – 50OA(I)/A5.7 – 50OA (■) and D2.2 – 50BA/A5.5 – 50BA (◆).

the general ability of interpolymer interaction between PDP and PAP increases with the content of functional groups and long chain alkyl acrylate unit, as well as the side chain length of alkyl acrylate unit in component polymers due

to van der Waals force between side chains in unlike macromolecular chains.

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