Macromolecules

Volume 25, Number 3 February 3, 1992

Complex Formation between Pairs of Vinyl Polymers

Neeta Tewari and A. K. Srivastava*

Department of Chemistry, H. B. Technological Institute, Kanpur, India

Received May 29, 1990; Revised Manuscript Received September 30, 1991

ABSTRACT: The coefficient of interaction (k_{AB}) between three pairs of polymers, viz., (i) poly(vinyl acetate) (PVAc) and poly(acrylonitrile) (PAN), (ii) poly(vinyl acetate) and poly(methyl methacrylate) (PMMA), and (iii) poly(vinyl acetate) and poly(methacrylic acid) (PMAA), has been determined at 60 °C in ternary solutions consisting of two polymers in DMSO, DMF, and dioxane by using the method of intrinsic viscosity measurement in a "polymer solvent". In these systems, where interpolymer complexes are formed, the coefficient of interaction (k_{AB}) value is extremely high, and it is a direct function of the polarity of the solvent used. The high k_{AB} values indicate that a strong interaction, which consists of van der Waals forces and hydrogen bonding, exists between the polymers.

The study of the viscosity of ternary solutions comprising a low molecular weight solvent and two chemically dissimilar polymers has been a subject of interest because it provides useful information regarding stereocomplex formation[1-3] between two polymers which is necessary for template polymerization. A search of the literature reveals that the values of k_{AB}, a term which provides information on the interaction of chemically dissimilar polymers and is similar to the Huggins coefficients k_A and k_B (originating from a superposition of several types of interactions, such as hydrodynamic and thermodynamic interactions), is available for a few systems only. For example, Moskowicz and Rosen[4] have determined the value of k_{AB} to be 0.27 for the polystyrene (A)–polybutadiene (B)–toluene system, while Hugelin and Dondos[5] have estimated the value of k_{AB} for the polystyrene–poly(methyl methacrylate)–xylene system.

The present paper, which is a continuation of our previous investigations,[6-8] using poly(vinyl acetate) as a template for the polymerization of acrylonitrile, methyl methacrylate, and methacrylic acid, describes the estimation of k_{AB} values and the nature of the stereocomplexation between the said polymers.

Experimental Section

Preparation of the polymer samples, their characterization, and the procedure used in the measurements have been reported in earlier papers[6-8] (Table I).

Solutions used in the viscosity measurements were prepared in the following way: The polymer, whose solution was used as the solvent, was dissolved to give a series of solutions having concentrations ranging from 2.5×10^{-4} to 10×10^{-4} g cm^{-3}. After dissolution and filtration, the second polymer (concentration 10×10^{-4} g cm^{-3}) was dissolved in these solutions.

To find out the strength of the interaction between the polymers, the interaction constant k_{AB} of a mixture of stereocomplexes of polymers (i.e., PVAc and PAN, PVAc and PMAA, and PVAc and PMMA) was evaluated.

Table I
Synthesis and Characterization of Template and Daughter Polymer

template[a] (PVAc) $\bar{M}_v$	PDI[e]	blank polymer	$\bar{M}_v$	PDI[e]	daughter polymer	$\bar{M}_v$	PDI[e]
47 090	2.67	PAN[b]	15 780	1.67	PAN	16 180	1.68
55 800	2.73	PMMA[c]	40 500	1.53	PMMA	43 800	1.56
66 400	2.81	PMAA[d]	20 000	1.37	PMAA	20 600	1.39

[a] [VA] = 3.6 mol L^{-1}, [AIBN] = 10^{-2} mol L^{-1}, temperature = 60 °C, η_{int} in benzene at 30 °C, $[\eta_{int}] = 22 \times 10^{-5}\bar{M}_v^{0.65}$. [b] [AN] = 1.88 mol L^{-1}, [BPO] = 0.0129 mol L^{-1}, temperature = 60 °C, [PVAc] = 0.8 base H, η_{int} in DMF at 30 °C, $[\eta_{int}] = 20.9 \times 10^{-5}\bar{M}_v^{0.75}$. [c] [MMA] = 2.94 mol L^{-1}, [AIBN] = 1.14×10^{-2} mol L^{-1}, [PVAc] = 2.90 base M, temperature = 60 °C, η_{int} in benzene at 30 °C $5.2 \times 10^{-5}\bar{M}_v^{0.76}$. [d] [MAA] = 0.78 mol L^{-1}, [PVAc] = 0.8 base M, [AIBN] = 2.38×10^{-2} mol L^{-1}, temperature = 60 °C. [e] PDI = polydispersity index. Waters GPC Model ALA 220, solvent THF, solvent flow = 2 mL/min, temperature = 27 °C.

In this study we describe the determination of the viscometric parameter k_{AB} at 60 °C, which characterizes mutual interaction between two polymers at this temperature as an analogy of a solution of a binary mixture of compatible polymers in a common solvent. For this purpose, the method of "polymer solvent" was employed.[9-14] According to this method, the intrinsic viscosity of the polymer A, $[\eta_A]_B$, is determined in a number of various concentrated solutions of polymer B which serve as solvents and vice versa. For $[\eta_A]_B$ we have

$$[\eta_A]_B = [\eta_A]/[\eta_r]_B(1 + 2k_{AB}[\eta_B]C_B + ...) \qquad (1)$$

where $[\eta_r]_B$ is the relative viscosity of the polymer B at the concentration C_B, and $[\eta_A]$ and $[\eta_B]$ are the intrinsic viscosities of the polymers A and B in a pure solvent. The constant k_{AB} is a criterion of interaction between macromolecules A and B. It may be obtained from the plot of f vs the reduced concentration

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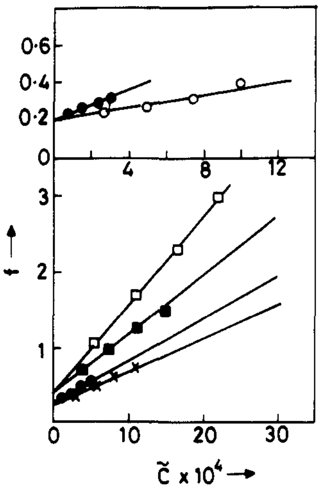


Figure 1. Dependence of the parameter f on the reduced polymer concentration $\tilde{C}$. Solution in DMSO: (□) PVAc solute, PAN solutions as solvents; (■) PAN solute, PVAc solutions as solvents. Solution in DMF: (X) PVAc solute, PAN solutions as solvents; (◐) PAN solute, PVAc solutions as solvents. Solution in dioxane: (○) PVAc solute, PAN solutions as solvents; (●) PAN solute, PVAc solutions as solvents.

Table II
Intrinsic Viscosities in Polymer Solvent (PVAc/PAN)

$C_{PAN} \times 10^4$, g cm^{-3}	$[\eta_{PVAc}]_{PAN}$, cm^3 g^{-1}	$C_{PVAc} \times 10^4$, g cm^{-3}	$[\eta_{PAN}]_{PVAc}$, cm^3 g^{-1}
	Solutions in DMSO		
0	1.50	0	2.20
2.5	5.50	2.5	6.80
5.0	7.20	5.0	8.50
7.0	10.48	7.5	10.60
10.0	14.50	10.0	11.75
	Solutions in DMF		
0	0.5	0	1.1
2.5	0.8	2.5	1.4
5.0	1.0	3.0	1.6
7.5	1.1	7.5	1.8
10.0	1.2	10.0	2.0
	Solutions in Dioxane		
0	0.3	0	1.0
2.5	0.6	2.5	1.1
5.0	0.8	5.0	1.3
7.5	1.0	7.5	1.5
10.0	1.1	10.0	1.7

Table III
Intrinsic Viscosities in Polymer Solvent (PVAc/PMMA)
($\bar{M}_v$(template) = 55 800)

$C_{PVAc} \times 10^4$, g cm^{-3}	$[\eta_{PMMA}]_{PVAc}$, cm^3 g^{-1}	$C_{PMMA} \times 10^4$, g cm^{-3}	$[\eta_{PVAc}]_{PMMA}$, cm^3 g^{-1}
	Solutions in DMF		
0	0.50	0	3.50
2.5	1.80	2.5	8.42
5.0	4.00	5.0	11.00
7.5	5.50	7.5	12.50
10.0	8.25	10.0	15.00
	Solutions in DMSO		
0	0.75	0	3.80
2.5	15.65	2.5	15.02
5.0	20.15	5.0	15.88
7.5	23.26	7.5	16.50
10.0	25.15	10.0	18.57

$\tilde{C} = [\eta_B]C_B$, giving directly k_{AB} from the intercept on the y axis. The case where the polymer B is the dissolved compound and the solution of the polymer A is the solvent is treated similarly and gives the same value ($k_{AB} = k_{BA}$).

The method of "polymer solvent" reflects changes in the molecular dimensions of the molecules of polymer A due to the molecules of polymer B and is more reliable and exact in the determination of k_{AB} than direct calculation of this value using the interaction constant obtained from measurements of the intrinsic viscosity of a solution of a mixture of polymers at a constant ratio of both components.

Results and Discussion

The ability of two polymers to form a complex depends upon the solvent, on the concentration ratio of the polymers in the mixture, on their total concentration, and on time. The present work, which describes the effect of solvents on the process of complex formation, has been carried out by the determination of k_{AB} values, which is associated with the interaction of unlike polymer molecules in the field of shear forces and is similar to the Huggins coefficients k_A and k_B. In general, the Huggins coefficient originates from a superposition of several types of interactions, the hydrodynamic and thermodynamic interactions being the most important. The thermodynamic contribution includes the intramolecular excluded volume effect, resulting in an expansion of the coil, and the intramolecular excluded volume effect, which results in contraction of the coil. The k_{AB} values characterizes the intensity of complexation in the different solvents, namely, DMSO, DMF, and dioxane. The experimental conditions and results have been summarized in Tables I–IV and Figures 1–4.

(i) Complex Formation between Poly(vinyl acetate) (PVAc) and Poly(acrylonitrile) (PAN). In Figure 1 the interaction parameter (*f*), defined as a measure of the hydrodynamic and thermodynamic interactions, is plotted as a function of $\tilde{C}$ in DMSO, DMF, and dioxane (Table II). The value of the mutual interaction coefficient k_{AB} (for the given system, A = PVAc and B = PAN) can be determined by extrapolating these lines to $\tilde{C} = 0$. A common intercept was obtained on the y axis, and $k_{AB} = k_{BA} = 0.40$ for DMSO, 0.25 for DMF, and 0.2 for dioxane. The k_{AB} values are low in comparison to those reported earlier.[4,5,17] These values indicate that the interaction between PVAc and PAN is weak and involves van der Waals forces. Study of Table II shows that the value of $[\eta_{PVAc}]_{PAN}$ increases as the concentration $\tilde{C}$ of PAN increases, significantly in DMSO and insignificantly in DMF and dioxane. This indicates that there is an increase in the dimension of the molecules of PVAc in the presence of PAN. It is therefore concluded that the molecular dimension increases significantly in DMSO and to a lesser extent in DMF and in dioxane. The high value of k_{AB} for DMSO ($\epsilon = 46.6$) in comparison to that of DMF ($\epsilon = 36.7$) and dioxane ($\epsilon = 2.2$) shows that the strength of complexation is stronger in DMSO, medium in DMF, and weaker in dioxane, and this seems to be related to the polarity or dielectric constant of the solvents. The strong interaction may be connected with the influence of the molecular weight of the components; e.g., the higher the molecular weight, the greater the number of interpolymer contacts and the stronger the interpolymer interaction.

(ii) Complex Formation between Poly(vinyl acetate) (PVAc) and Poly(methacrylic acid) (PMAA). The condition for obtaining the coefficient k_{AB} (for the given system, A = PVAc and B = PMAA) from the viscometric measurements, as described above, is a linear dependence of the intrinsic viscosity of the solution of the polymer mixture on the weight fractions of the polymer components (additivity of their intrinsic viscosities). The results are listed in Table IV and shown in Figure 3. From Figure 3 it is clear that *f* is a direct function of $\tilde{C}$, and the values of the mutual interaction coefficients, $k_{AB} = k_{BA}$, obtained in DMSO and DMF are 1.4 and 0.5, respectively.

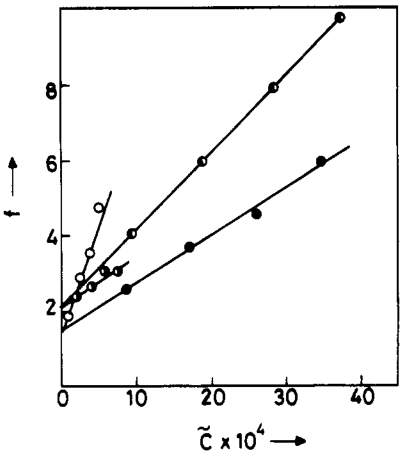


Figure 2. Dependence of the parameter f on the reduced polymer concentration $\tilde{C}$. Solution in DMSO: (◑) PVAc as solute, PMMA solutions as solvents; (◐) PMMA as solute, PVAc solutions as solvents. Solution in DMF: (○) PVAc as solute, PMMA solutions as solvents; (●) PMMA as solute, PVAc solutions as solvents.

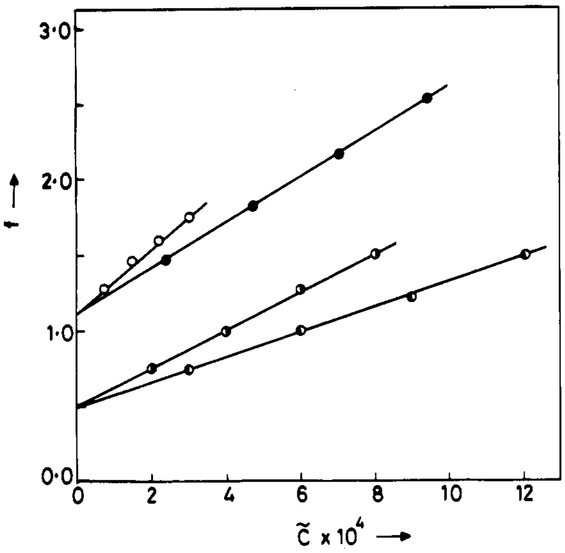


Figure 3. Dependence of the parameter f on the reduced polymer concentration $\tilde{C}$. Solution in DMSO: (●) PVAc as solute, PMMA solutions as solvents; (○) PMAA as solute, PVAc solutions as solvents. Solution in DMF: (◐) PVAc as solute, PMAA solutions as solvents; (◑) PMAA as solvents, PVAc solutions as solvents.

Table IV
Intrinsic Viscosities in Polymer Solvent (PVAc/PMAA) ($\bar{M}_v$(template) = 66 400)

$C_{PVAc} \times 10^4$, g cm^{-3}	$[\eta_{PMAA}]_{PVAc}$, cm^3 g^{-1}	$C_{PMAA} \times 10^4$, g cm^{-3}	$[\eta_{PVAc}]_{PMAA}$, cm^3 g^{-1}
	Solutions in DMSO		
0	0.95	0	0.300
2.5	1.200	2.5	0.325
5.0	1.425	5.0	0.350
7.5	1.620	7.5	0.375
10.0	1.800	10.0	0.400
	Solutions in DMF		
0	1.20	0	0.30
2.5	1.46	2.5	0.90
5.0	1.68	5.0	1.40
7.5	1.86	7.5	1.66
10.0	1.98	10.0	1.80

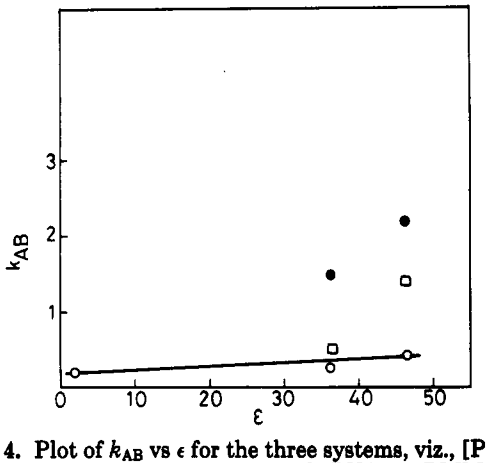
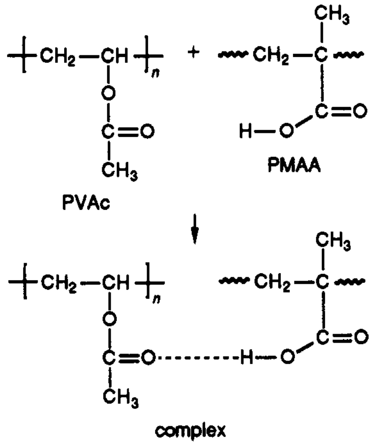
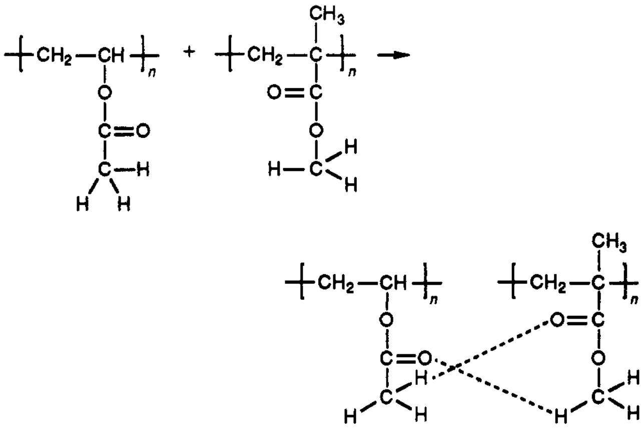


Figure 4. Plot of k_{AB} vs ε for the three systems, viz., [PVAc vs PAN] (○), [PVAc vs PMMA] (●), and [PVAc vs PMMA] (□).

The values of k_{AB} are much higher than reported earlier.[13] These values show that the interaction between PVAc and PMAA involves hydrogen bonding in addition to van der Waals forces. Study of Table IV indicates that the value of $[\eta_{PVAc}]_{PMAA}$ increases as the concentration $\tilde{C}$ of PMAA increases, signicantly in DMSO and insignificantly in DMF. This indicates that there is an increase in the dimension of the molecules of PVAc in the presence of PMAA. It is concluded that the molecular dimension increases significantly in DMSO, and less in DMF. Therefore, the k_{AB} values are larger for DMSO than for DMF, and this can be related to the solvent dielectric constant. Since poly(methacrylic acid) is insoluble in dioxane, the k_{AB} was not determined in dioxane. The interaction between PVAc and PMAA molecules is stronger than between PVAc and PAN molecules. A possible structure for the complex is



(iii) Complexation Formation between Poly(vinyl acetate) (PVAc) and Poly(methyl methacrylate) (PMMA). Complex formation between PVAc and PMMA has been studied, and the results are illustrated in Table III and shown in Figure 2. It is clear that f is a direct function of $\tilde{C}$; i.e., the complexation is strong. The value of the interaction coefficient k_{AB} (for the given system, A = PVAc and B = PMMA) was determined by extrapolating these lines to $\tilde{C} = 0$; a common intercept was obtained on the y axis, and k_{AB} (=k_{BA}) was equal to 2.2 for DMSO and 1.5 for DMF. The value of k_{AB} for dioxane was not calculated since PMMA is insoluble in dioxane. Therefore, in Figure 4, only two points are shown. The values of k_{AB} are much higher than the values reported earlier. These values show that the interaction between PVAc and PMMA involves more hydrogen bonding in addition to van der Waals forces. (This is supported by the structure of the complex given below.) From Table III, it is clear that the value of $[\eta_{PVAc}]_{PMMA}$ increases as the concentration $\tilde{C}$ of PMMA increases significantly in DMSO and insignificantly $\tilde{C}$ of PMMA increases significantly in DMSO and insignificantly in DMF. This indicates that there is an increase in the dimension of the molecules of PVAc in the presence of PMMA. It is therefore concluded that the molecular dimension increases significantly in DMSO and less in DMF. The high value of k_{AB} for DMSO is comparison to that of DMF shows that the strength of complexation is stronger in DMSO than in DMF, and this seems to be related to the high polarity or dielectric constant of the solvent. A possible structure may be A:



A

From the data it can be concluded that the k_{AB} values obtained are unusually high. This behavior has been assigned to the expansion of the coil, which depends upon the intramolecular excluded volume effect, a thermodynamic contribution. The k_{AB} coefficients reported in the literature[13] for pairs of (the usual) common polymers are much lower (0.2–0.3). The difference can be explained only by exceptionally strong interactions between the components of the polymer pair used in the above system. The lower k_{AB} value for the solution in dioxane and DMF compared with that in DMSO is in agreement with the weaker complex formation.

Acknowledgment. We thank Prof. A. K. Vasishtha, Director, and Prof. R. S. Tewari, Head, Chemistry Department, H. B. Technological Institute, Kanpur, for encouragement. Financial assistance by D.S.T. New Delhi for the project (SP/S1/GO8/85) is gratefully acknowledged.

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