Macromolecules **1990,** *23,* 5359–5361

Comments on Thermal Transitions in Some Polyelectrolyte Complexes

MALCOLM B. HUGLIN,* JOSE M. REGO, AND SHABAN R. GOODA

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Received December 1, 1989;
Revised Manuscript Received May 25, 1990

Introduction

In a previous paper,[1] we reported on the behavior of polymer blends based on the basic polymers poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) with poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS). When solutions of these polymers were mixed, a precipitate appeared. This precipitation was attributed to the formation of an effective cross-linking, which prevents chain expansion and subsequent reorientation of the chains in order to minimize the strong electrostatic repulsions between pyridinium groups. Characterization of the blends by differential scanning calorimetry (DSC) showed that (i) the glass transition temperatures T_g of the complex were much higher than those of the individual components and (ii) the values of T_g for the complex were influenced by the molar masses of the constituent compounds. However, the range of molecular masses studied was rather narrow. In the previous work it was also noted that there was a difference between the actual weights of the precipitates and the weights calculated on a stoichiometric basis.

In the present paper the aim is to extend the studies to include wide variations in the molar masses of both P2VP and PAMPS and to examine not only the weights but also the composition of the polyelectrolyte complexes produced.

Experimental Section

Aqueous solutions of AMPS (Sigma Chemical Co.) and ammonium persulfate were outgassed with gaseous nitrogen for 1 h prior to polymerization at 323 K. Unreacted monomer was removed by dialysis with deionized water for 3 days, and PAMPS was obtained in a white powder form by freeze-drying and final drying in a vacuum oven at 314 K for 24 h. For polymerization times of ca. 30 min, changes in molar mass were effected by changes in initial ratios of the concentration of monomer to initiator, and the actual molar masses were determined from the limiting viscosity number (LVN) measured in 5 M aqueous NaCl at 298 K in conjunction with the Mark–Houwink–Sakurada (M–H–S) constants.[2] The molar masses of samples designated PAMPS-1, PAMPS-2, PAMPS-3, and PAMPS-4 are given in Table I.

The preparation of the sample designated P2VP-2 has been described in our earlier report.[1] Its molar mass was determined to be 1.6×10^5 g mol^{-1} from the measured LVN in methanol at 298 K in conjunction with published M–H–S constants.[3] Samples of P2VP of quoted molar masses 0.4×10^5 and 3.0×10^5 g mol^{-1} were also purchased from Polyscience Ltd. These samples from Polyscience will be denoted P2VP-1 and P2VP-3, respectively.

The blends for the analysis of the T_g dependence with molar mass were prepared by adding stoichiometrically the appropriate volumes of PAMPS solution (having a concentration of 10 g dm^{-3}) to the P2VP solution (having a concentration of 20 g dm^{-3}). The solvent medium used was a 30/70 (v/v) water/ethanol mixture. The possible combinations of the different molar masses were selected in order to encompass the widest possible range.

The blends for the gravimetric analysis were made by mixing separate solutions of both components (P2VP-3 and PAMPS-1 were selected for this determination). The concentrations of the PAMPS and P2VP solutions were 14 and 20 g dm^{-3}, respectively.

Table I
Thermal Transition Temperatures (K) of Blends of P2VP (T_g = 368–376 K) with PAMPS (T_g = 348 K)[a]

	PAMPS-1 (530)	PAMPS-2 (680)	PAMPS-3 (960)	PAMPS-4 (4000)
P2VP-1 (30)	408	428	428	444
P2VP-2 (165)	430			
P2VP-3 (300)	444	436	447	453

[a] Molar masses (kg·mol^{-1}) of the precursors are given in parentheses.

Six different mole fractions of AMPS units X_{AMPS} in the total initial solutions of P2VP and PAMPS were prepared: 0.9, 0.8, 0.7, 0.6, 0.5, and 0.2. The precipitates were isolated by centrifugation and washed with aqueous ethanol prior to drying to constant weight in a vacuum oven at 313 K. For the composition analysis, the concentration of PAMPS in the supernatant liquids was analyzed via conventional titration techniques.

DSC measurements were made with a Mettler TA-3000 instrument, which was previously calibrated with indium. The glass transition temperatures (T_g) were determined by using a heating rate of 10 K/min and the middle-point criterion. All the samples were subjected to the same thermal treatment, i.e., 10 min at 423 K.

Results and Discussion

Dependence of the Glass Transition on Molar Masses of the Components. The characterization of the precipitates obtained on pouring PAMPS solutions into P2VP solutions showed strong electrostatic interactions between the pyridinium ring in P2VP and P4VP and the sulfonate group in PAMPS which bring about an effective physical cross-linking.[1] The meaning of the glass transition in this case must be, therefore, carefully established, since the precipitates are not linear polymers. The state above the "glass transition" for these precipitates can be defined as a "liquid with physically fixed structure" using the nomenclature by Ueberreiter and Kanig,[4] and the whole system can be modeled as a mesh with a large number of physical cross-links. Although the DSC thermograms for both precursors and complexes were of the form typical of a glass/rubber transition and the symbol T_g is used here, the previous comments indicate that it might well be more appropriate to refer to the relevant transitions less specifically as thermal ones. Table I summarizes the results obtained for the "glass transitions" of the different blends studied here. These results fully corroborate those presented in the previous paper and, furthermore, indicate the following features: (i) The effect of molar mass is more apparent when one of the components is of low molar mass, e.g., P2VP-1; (ii) the same change in T_g (36 K) is observed for the blends PAMPS-1/P2VP-3 and PAMPS-4/P2VP-1, thus indicating that it is possible to obtain similar changes by two different approaches, viz., either when both components are of similar and fairly high molar mass (PAMPS-1/P2VP-3) or when a low molar mass polymer and one of very high molar mass (PAMPS-4/P2VP-1) are used.

It is well-known that chemical cross-linking gives rise to an increase of the T_g and to the widening of this transition. If we consider the thermodynamic approach of the T_g, this transition takes place when the configurational entropy (S_c) becomes zero.[5] Using DiMarzio's terminology, we can write

$$S_c = S_0 + \Delta S_1 \qquad (1)$$

where S_0 is the configurational entropy for the un-cross-linked polymer and ΔS_1 is the change in configurational entropy due to adding cross-links. The effect associated with the addition of cross-links is a reduction of the

0024-9297/90/2223-5359$02.50/0

configurational entropy and, therefore, a cross-linked polymer on being cooled reaches the glass transition condition, viz., $S_c = 0$ at a higher temperature; that is, the T_g for the cross-linked polymer is higher than the corresponding one for the linear polymer. On this basis, DiMarzio[5] derived an equation that gives the temperature increment as a function of cross-linking density:

$$[T(\chi) - T(0)]/T(0) = (KM\chi/\gamma)/[1 - (KM\chi/\gamma)] \quad (2)$$

where $T(\chi)$ is the T_g for the cross-linked polymer, $T(0)$ is the T_g of the linear un-cross-linked polymer, M is the monomer molar mass, γ is the number of flexible bonds per monomer, χ is the number of cross-links per gram, and K is a constant independent of the material (1.25×10^{-23}) which is asserted to be dimensionless but which actually appears to have units of moles.

According to this equation, the greater the value of χ, the larger is the increment $T(\chi) - T(0)$, i.e., a higher glass transition temperature is associated with a higher degree of cross-linking. For the present systems, calculation via eq 2 using experimental values of $T(\chi) - T(0)$ and taking P2VP as the initial polymer prior to its incorporation into a cross-linked network with AMPS shows that the values of χ are in the range 1.15×10^{20} to 2.5×10^{20} g^{-1} (in 1 g of precipitate formed from solutions of PAMPS and P2VP for which X_{AMPS} is 0.5, the number of AMPS units is ca. 1.4×10^{21}, which indicates the presence of uncomplexed moieties). The thermodynamic view of the relation between the T_g and cross-linking allows us to draw a feasible explanation for the findings pointed out in our previous paper, viz., the higher T_g observed for the complex than for the individual components. The influence of molar mass can be rationalized qualitatively on the basis of the effect of chain ends, which increase in concentration with decrease in the molar mass. In principle, a larger concentration of chain ends implies a higher number of degrees of freedom and, therefore, a higher configurational entropy S_c, which, as indicated before, is related to a lower T_g.

Composition of the Precipitates. The combination of titration, in order to determine the remaining amount of PAMPS in the supernatant liquid, and gravimetric analysis of the precipitates enables the mole fraction of AMPS units in the precipitate X_{AMPS}^* to be calculated readily. As mentioned in the Experimental Section, this analysis was conducted on blends formed by P2VP-3 and PAMPS-1. Figure 1a shows the variation of the quantity $(W_a - W_{calc})/W_{calc}$ with the mole fraction of AMPS units X_{AMPS} in the total initial solutions of PAMPS and P2VP. The actual weight of the precipitate is denoted by W_a, whereas W_{calc} is the weight calculated on the basis of exact stoichiometry between the interactive units. The variation of the quantity $(W_a - W_{calc})/W_{calc}$ with X_{AMPS} is very similar to that reported and discussed previously[1] for the combination of PAMPS-1 with a poly(2-vinylpyridine) of molar mass smaller than that of the P2VP-3 used here. Hence, there is no apparent influence of molar mass. The variation of X_{AMPS}^* with X_{AMPS} is shown in Figure 1b. As can be observed from this figure, for $X_{AMPS} = 0.2$ and 0.5 both X_{AMPS} and X_{AMPS}^* have the same value, while values of $X_{AMPS} > 0.5$ are associated with $X_{AMPS}^* \simeq 0.5$. Combining this information with that provided by Figure 1a, one can draw a plausible explanation for this behavior.

When $X_{AMPS} = 0.2$, $(W_a - W_{calc})/W_{calc}$ is ca. 0.75 and X_{AMPS}^* is ca. 0.2, which indicates that a small content of the acid is able to precipitate more P2VP than the stoichiometrically calculated value. However, further addition of the acid is accompanied by increasing content of AMPS units within the precipitate and by $(W_a - W_{calc})/W_{calc}$ values close to the stoichiometric ones. For $X_{AMPS} > 0.5$, X_{AMPS}^* remains practically constant. These results show therefore that in the first stages of complexation the content of P2VP is higher than the stoichiometric value, this being related to a high concentration of free pyridine groups in the precipitate. Subsequent addition of PAMPS complexes not only pyridine groups available in the solution but also the free pyridine groups present on or in the precipitate. For $X_{AMPS} \simeq 0.5$, both $(W_a - W_{calc})/W_{calc}$ and X_{AMPS}^* show that the concentration of reacted pyridine groups is close to the stoichiometric value, since the former is ca. 0 and the latter 0.5. Hence, for $X_{AMPS} > 0.5$ no further precipitation occurs, and the extra PAMPS added remains in solution. The observation that X_{AMPS}^* values are slightly higher than 0.5 for X_{AMPS} between 0.5 and 0.9 is due to the existence of free sulfonic acid groups. The presence of unreacted moieties in the polyelectrolyte complex, either pyridine or sulfonic acid groups, must be due to restricted accessibility. Indeed we have demonstrated elsewhere[6] that it is difficult to achieve complete protonation of P2VP by strong acids.

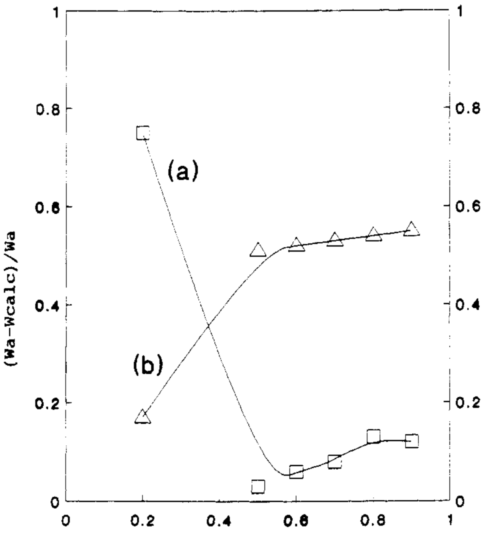

Figure 1. (a) Change of $(W_a - W_{calc})/W_{calc}$ with the mole fraction of AMPS units X_{AMPS} in the total initial solutions of P2VP and PAMPS. (b) Variation of the mole fraction of AMPS units X_{AMPS}^* in the precipitate with X_{AMPS}.

Hence, as seen here and noted also in our previous related work[1] on these types of polyelectrolyte complexes, departure from 1:1 stoichiometry can occur at certain compositions of the precursor mixture, the product being a precipitated complex. This behavior is rather unusual since, as observed by Tsuchida et al.[7] and later by Kabanov et al.,[8,9] deviation from stoichiometry is certainly much more prevalent in macroscopically homogeneous system, i.e., soluble complexes. However, nonstoichiometric precipitated polyelectrolyte complexes are not without precedent, the relatively small number of previous reported examples being discussed by Philipp et al.,[10] who proposed feasible explanations specific to each system. Among these the only one of possible applicability to the present system is inactivation of ionic groups due to protonation or deprotonation of anionic and cationic groups, respectively. Clearly, with regard to stoichiometry, the overall situation is not yet at a point of unequivocal rationalization.

Finally, it is important to note that the results reported on these polyelectrolyte complexes are unaffected by the order of addition (i.e., P2VP to PAMPS or vice versa).

Acknowledgment. J.M.R. thanks the Ministerio de Educación y Ciencia of the Spanish Government for the provision of a research fellowship. Financial support (to S.R.G.) from the Egyptian Government is gratefully acknowledged.

References and Notes

(1) Huglin, M. B.; Rego, J. M. *Polymer* **1990**, *31*, 1269.
(2) Fisher, L. W.; Sochor, A. R.; Tan, J. S. *Macromolecules* **1977**, *10*, 949.
(3) Arichi, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 439.
(4) Ueberreiter, K.; Kanig, G. *J. Chem. Phys.* **1950**, *18*, 399.
(5) DiMarzio, E. A. *J. Res. Nat. Bur. Stand.* **1964**, *68A*, 611.
(6) Rego, J. M.; Huglin, M. B.; Gooda, S. R. *Br. Polym. J.* **1990**, *23*, 333.
(7) Tsuchida, E.; Osada, Y.; Sanada, K. *J. Polym. Sci., Part A-1* **1972**, *10*, 3397.
(8) Kabanov, V. A.; Zezin, A. B. *Pure Appl. Chem.* **1984**, *56*, 343.
(9) Charenko, O. A.; Charenko, A. B.; Kasaikin, V. A.; Zezin, A. B.; Kabanov, V. A. *Vysokomol. Soedin. A* **1979**, *21*, 2726.
(10) Philipp, B.; Dautzenberg, H.; Linow, K.-J.; Kotz, J.; Dawydoff, W. *Prog. Polym. Sci.* **1989**, *14*, 91.

Registry No. P2VP (homopolymer), 25014-15-7; PAMPS (homopolymer), 27119-07-9.