Formation of polyvinylpyrrolidone–syndiotactic poly(methacrylic acid) complexes in dimethylformamide

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Interpolymer complex formation between polyvinylpyrrolidone and syndiotactic poly(methacrylic acid) has been studied using dimethylformamide as solvent. Compact and globular complex particles are formed, with equimolar composition. The increase of compactness of the particles on raising the temperature as well as the volume expansion on mixing solutions of component polymers indicate that the complexation is predominantly determined by desolvation. In this connection, it may be assumed that besides the cooperative hydrogen bonding force between the polymers some kind of 'solvophobic interaction' between segments of the polymer complex determines the ultimate structure of the complex.

INTRODUCTION

Hydrogen bonding between complementary polymers like poly(acrylic acid) or poly(methacrylic acid) (PMAA) and polyvinylpyrrolidone (PVP) leads to very stable interpolymer complexes in a number of solvents[1-7]. In water, hydrophobic interaction acts as an extra stabilizing factor in the complexation of PMAA and PVP[8-12]. Such polymer complexes are generally produced on mixing solutions of both component polymers. Alternatively, these complexes can be formed *in situ* during a template polymerization process[3,6,13].

While most authors neglect the influence of tacticity of the component polymers on the complexation behaviour, Bartels *et al.*[3] showed that in dimethylformamide (DMF) syndiotactic (st-)PMAAs gave the strongest complexes with PVP. Therefore, a closer investigation was carried out on the template polymerization of *N*-vinylpyrrolidone (*N*VP) in the presence of PMAA of high syndiotactic content[13]. From the kinetic results we suggested the occurrence of a desolvation process, whereby st-PMAA chains which are thought to be highly solvated in DMF, are desolvated during propagation of PVP-chain radicals along them. The entropy gain as a consequence of this process, would compensate for the usually observed loss of overall activation entropy, $\Delta S^{\ddagger}$ during template reactions[14,15]. To support this idea of desolvation, experiments on PVP/st-PMAA complexation in DMF were undertaken, the results of which are presented in this paper.

EXPERIMENTAL

Materials

Polymethacrylic acid: The synthesis, purification and characterization of st-PMAA samples were described in a previous paper[13]. Data on the PMAAs used are presented in *Table 1*.

Polyvinylpyrrolidone: Commercial PVP K90 (BASF, Kollidon) was reprecipitated twice from chloroform solution in diethylether. A high molar mass fraction was obtained with $\bar{M}_v$ of 640000, according to the relationship[16] $[\eta]=1.4\times10^{-4}\times\bar{M}_v^{0.7}$ in water at 30°C. PVP of a much lower molar mass (PVP 21) was synthesized by free radical polymerization of 0.75 M *N*VP in DMF at 60°C, using 0.01 M azobisisobutyronitrile (AIBN) as initiator; the conversion was 50% after 3 h. This PVP 21 was used in many experiments, as its $\bar{M}_v$ of ~36000 was much nearer the $\bar{M}_v$ of the PVP formed during template polymerizations[13].

Further reagents: Dimethylformamide (Merck p.a., dried over P_2O_5) and *N*-vinylpyrrolidone (Fluka p.a.) were distilled under reduced N_2-pressure before use. AIBN was recrystallized from methanol.

Techniques

Viscometry: the reduced viscosity of each component polymer or complex solution was measured in an Ubbelohde viscometer. By variation of the capillary diameters the dependence of reduced viscosity on shear rate was investigated. In the temperature dependent experiments the solutions of the component polymers in DMF were preheated at the desired temperature and then mixed in a 1/1 molar ratio, so that the viscosity could be

Table 1 Characterizations of st–PMAAs

Code PMAA	$\bar{M}_v^* \times 10^{-3}$	Triad tacticity I	H	S
st–117	193	1	7	92
st–118	205	0	3	97
st–125	67	0	7	93
st–130	158	0	5	95

* Determined as PMMA in chloroform at 25°C; $\bar{M}_v$ (PMAA) = 0.86 x M_v (PMMA)

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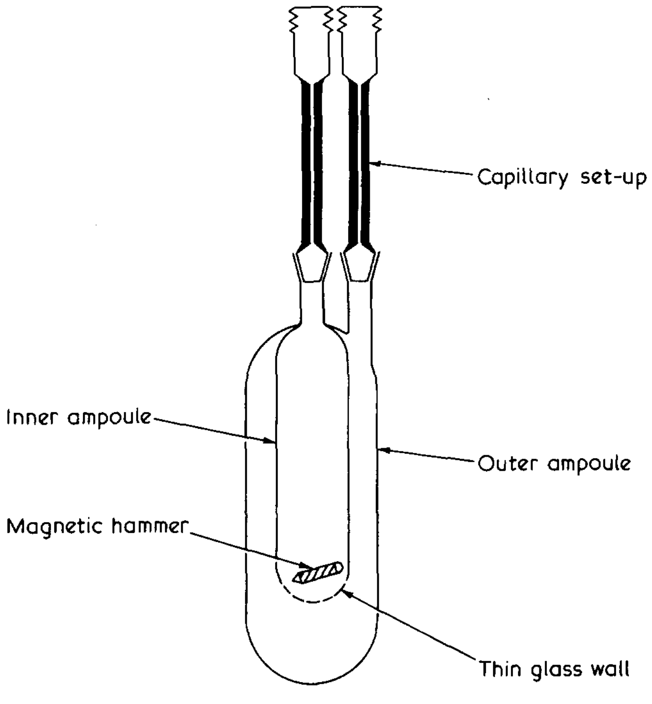

Figure 1 **Schematic drawing of mixing dilatometer**

determined immediately after mixing. In another series of experiments a stable polymer complex solution formed at room temperature during at least 20 h was heated and kept at the desired temperature until no further change in viscosity could be observed.

Light scattering: for equilmolar PVP/st–PMAA solutions in DMF, the intensity of the scattered light at an angle of 90°, I_{90}, was measured as a function of temperature with a CENCO–TNO Light Scattering Meter. An Original Hanau (st 75) high pressure mercury lamp ($\lambda = 546.1$ nm) was used as light source.

The weight average molar mass of complex particles was estimated from laser light experiments, using a Malvern Light Scattering Photometer, coupled with a NEC He–Ne laser light source ($\lambda = 633$ nm). Solutions of the component polymers were filtered through a glass filter and centrifuged at 18 000 rpm during 2 h. A complex solution (0.25 g dl^{-1}) was then prepared by filtering equimolar quantities of PVP and st–PMAA in DMF through a membrane filter into the measuring cell. The intensity of the scattered light was measured between 30 and 140°; it increased 15–20% over a one day period, reaching a stable value by then. Other concentrations were made by further dilution with dust free DMF. The refractive index increment, dn/dc, of the complex in DMF was determined with a Zeiss–Jena interferometer.

Electron microscopy: the size of complex particles formed in DMF solution was estimated from transmission electron micrographs. Complex solutions (0.025%, w/v) were sprayed on grids after which the solvent was removed quickly at 50°C *in vacuo*. The samples were then shadowed with platinum.

Mixing dilatometry: the volume change on mixing PVP and st–PMAA solutions in DMF or DMF/NVP mixtures was measured at 60°C in a special 'mixing dilatometer' as illustrated in *Figure 1*.

Polymer solutions were brought separately into the inner and outer ampoule and degassed thoroughly. After immersion in a thermostatically controlled bath, the liquid level in both ampoules was brought up to a readable level in the capillary set-up. Then the thin glass bottom of the inner ampoule was broken with a magnetic hammer and after temperature equilibration the new level could be read. Mixing of the solutions was performed with an air driven magnetic stirrer placed in the bath, while the hammer functioned as stirrer.

Pycnometry: the specific volumes of component polymers or polymer mixtures in DMF were measured in a common type pycnometer at 60°C.

RESULTS

Viscometry

When the reduced viscosity, $\eta_{sp/c}(=\eta_{red})$, of mixtures of PVP and syndiotactic PMAA in DMF is measured as a function of composition, *Figure 2* is obtained.

A rather sharp minimum in η_{red} can be observed at 43.65 wt% st–PMAA, corresponding to a 1/1 base molar composition. All experimental points were determined about $1\frac{1}{2}$ min after mixing the components at 25°C, the time needed for complete mixing and filling of the Ubbelohde viscometer. A rapid decline of viscosity with time was observed as exemplified by an equimolar mixture (*Figure 3*). The ultimate level after at least 20 h, is indicated in *Figure 2* by filled dots.

The dramatic drop in viscosity relative to the additive value for PVP and st–PMAA in DMF indicates that very compact particles are formed. From an observed independence of reduced viscosity on shear rate it is suggested that we are dealing with globular complex particles.

Furthermore, η_{red} was not affected by variation of the complex concentration in DMF as can be deduced from *Figure 4*. In order to be sure of optimal complexation behaviour, all experiments were carried out with complex solutions aged for at least 24 h.

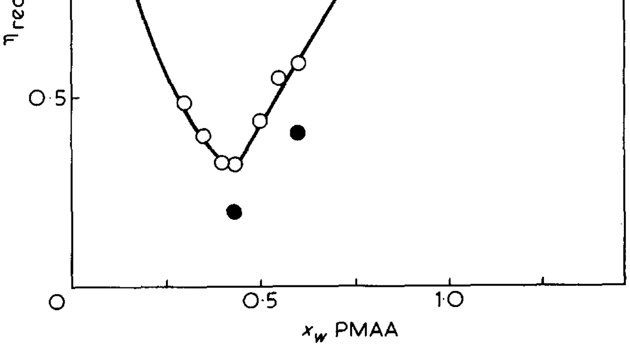

Figure 2 **Reduced viscosity, η_{red}, *versus* st–PMAA weight fraction, x_w, for PVP/st–PMAA mixtures in DMF, 1.5 min, (○) and >20 h, (●) after mixing; additivity line (— — — —). [PVP K90] + [st–PMAA 118] = 0.25 g dl^{-1}, temperature = 25°C**

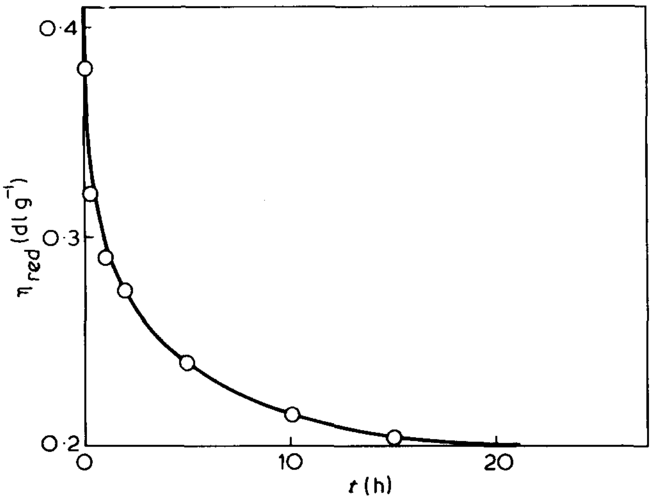

Figure 3 Reduced viscosity, η_{red}, *versus* time after mixing, t, for 1/1 PVP/st–PMAA complex in DMF. [PVP K90] + [st–PMAA 118] = 0.25 g dl^{-1} temperature = 25°C

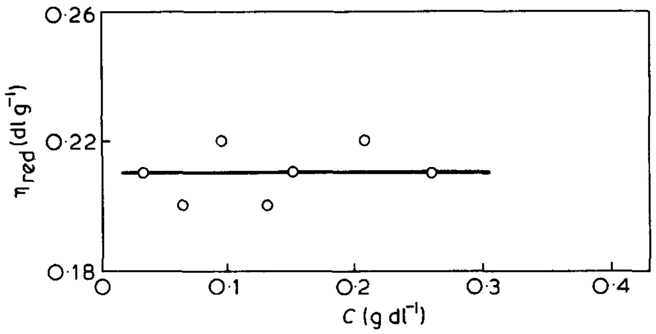

Figure 4 Reduced viscosity, η_{red}, *versus* 1/1 PVP K90/st–PMAA 117 complex concentration, c, in DMF; temperature = 25°C

The very low value of the reduced viscosity of equimolar PVP/st–PMAA complexes in DMF decreases even more when the temperature is raised up to 80°C, after which it gradually increases. When we compare the experimental reduced viscosity with the additive value for both component polymers this effect is even more pronounced. This is illustrated in *Figure 5* with:

$$\Delta\eta_{red} \equiv \frac{(\eta_{red.exp.} - \eta_{red,add.})}{\eta_{red,add.}} \times 100$$

where $\eta_{red,exp.}$ and $\eta_{red,add.}$ are the observed and additive reduced viscosity, respectively.

Temperature increase apparently causes stronger complex formation resulting in further particle shrinkage. Above 80°C the complexes start to expand.

Light scattering and electron microscopy

From the viscometric behaviour it can be concluded that the compact spherical complex particles possess a dense packing of polymer segments (see Discussion). The same conclusion can be drawn from measurement of turbidity of the complex solution as a function of temperature (*Figure 6*). The positive turbidity increment demonstrates a more dense packing of complex chains within the particles. Above about 85°C a reversible loosening of structure occurs, while at still higher temperatures (> 115°C), slow irreversible dissociation or decomposition takes place.

Owing to the dense segmental packing of the chains it is possible that many PVP and st–PMAA chains constitute one complex particle in DMF as is the case in complexes of at–PMAA with PVP or polyethyleneoxide in water[1,5]. This may be tested by determining $\bar{M}_w$ using light scattering. Furthermore, information about the particle size may be obtained through the radius of gyration, *Rg*. However, a rather strange scattering behaviour was observed.

According to the Rayleigh scattering theory, the intensity of the scattered light should decrease with angle, but the opposite occurred. Therefore, only very unusual Zimm plots could be drawn (*Figure 7*) from which no *Rg*-values could be derived. An apparent molar mass, $\bar{M}_{w,app.}$ of about 10×10^6 was calculated. Zimm plots with such an inverse intensity increment were also obtained using a

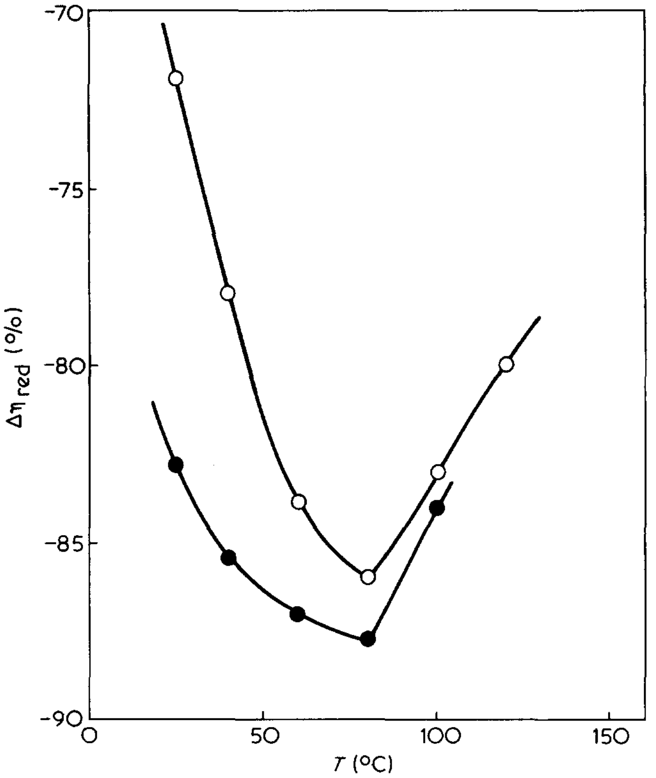

Figure 5 Relative change in reduced viscosity, $\Delta\eta_{red}$, *versus* temperature for 1/1 PVP/st–PMAA complex in DMF; values 1.5 min, (○) and >20 h, (●) after mixing. [PVP K90] + [st–PMAA 117] = 0.25 g dl^{-1}

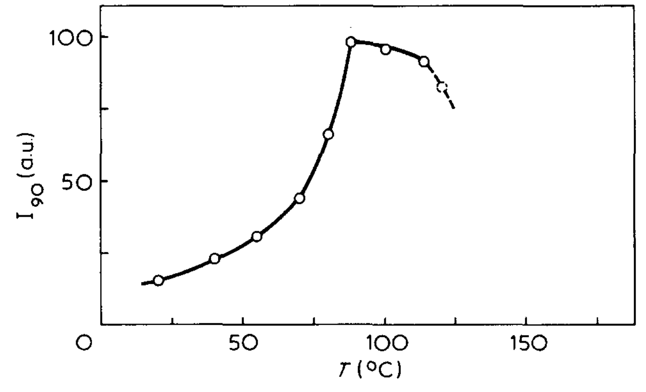

Figure 6 Intensity of scattered light at 90° angle, I_{90}, *versus* temperature for 1/1 PVP/st–PMAA complex in DMF. [PVP 21] + [st–PMAA 130] = 0.25 g dl^{-1}

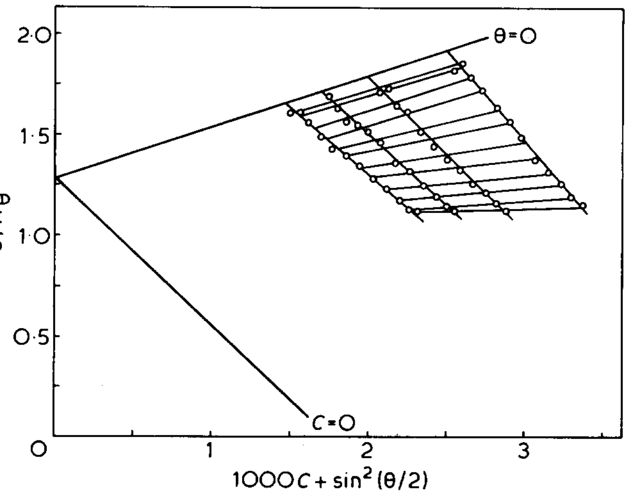

Figure 7 **Zimm plot of PVP 21/st–PMAA 130 complex in DMF at 25°C**

Fica Photo-gonio-diffusometre 42000 M ($\lambda = 546$ nm). Moreover, an analogous behaviour could be seen when PVPs or st–PMAAs of other molar masses were used.

Figure 8 shows an electron micrograph from which one can deduce the presence of particles of a rather uniform diameter of ~70 nm. An estimation of the original particle size in solution is hard to make from this figure as the particles must have shrunk on drying and even seem to have flattened (almost no shadows appeared).

Mixing volume

From the foregoing results we may expect that formation of compact PVP/st–PMAA particles would involve some shrinkage of the total volume. However, the opposite appeared to be true. Evidences for the occurrence of volume expansion on complexation were obtained from the following techniques:

Dilatometry[13]: Rate constants for the polymerization of NVP in the presence and absence of st–PMAA were derived from dilatometric rate measurements by using conversion factors defined as the weight of converted monomer per cm^3 volume shrinkage. For template and blank polymerizations values of 6.2 and 5.7 g cm^{-3} were found, respectively. The higher value means that the volume shrinkage during template polymerizations is less than that of blank ones. Assuming identical densities for PVP in both types of polymerization, the difference can be attributed to a 'hidden' volume increase during template polymerizations which may be caused by desolvation of st–PMAA during propagation of PVP-radicals along the polyacid. From the difference in conversion factors a volume expansion per mass unit of complexating PVP of 0.014 cm^3 g^{-1} can be calculated.

Mixing dilatometry: In a mixing dilatometer as described in the Experimental section we were able to determine the volume change $\Delta V_{\rm mix}$, during the mixing of solutions of PVP and st–PMAA in DMF and DMF/NVP mixtures. In order to avoid gel formation within the ampoules which may lead to incomplete complex formation, rather low polymer concentrations (± 1 wt%) were used. In some experiments 1 wt% of NVP was added to the DMF solutions to simulate the polymerization conditions. In both cases a volume expansion, $\Delta V_{\rm mix}$, of 0.016 cm^3 g^{-1} PVP was found.

Pycnometry: Specific volume measurements of PVP and st–PMAA solutions and mixtures of both polymers were performed in a pycnometer, using one total polymer concentration of 4.73 wt%. In this way the ternary mixture PVP, st–PMAA, DMF can be considered as a quasi-binary system. Rather low molar mass st–PMAA 125 was used in order to prevent incomplete mixing by gel formation. If there is no volume change during mixing c.q. complexation, the specific volume would be strictly additive and the course of the resultant specific volume as a function of composition can be represented by a straight line (*Figure 9*, broken line). On the contrary, measured points fell above this additivity line, signifying a positive mixing volume. The volume expansion was maximal at an equimolar composition of the polymer mixture and correlated with a $\Delta V_{\rm mix}$ of 0.013 cm^3 g^{-1} PVP which is approximately identical with the previous values.

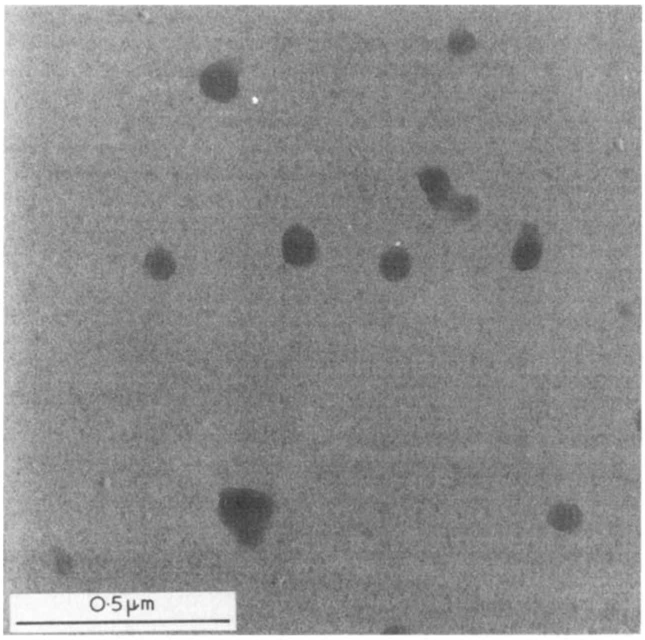

Figure 8 **Transmission electron micrograph of 1/1 PVP 21/st–PMAA 130 complex from 0.025 g dl^{-1} DMF solution**

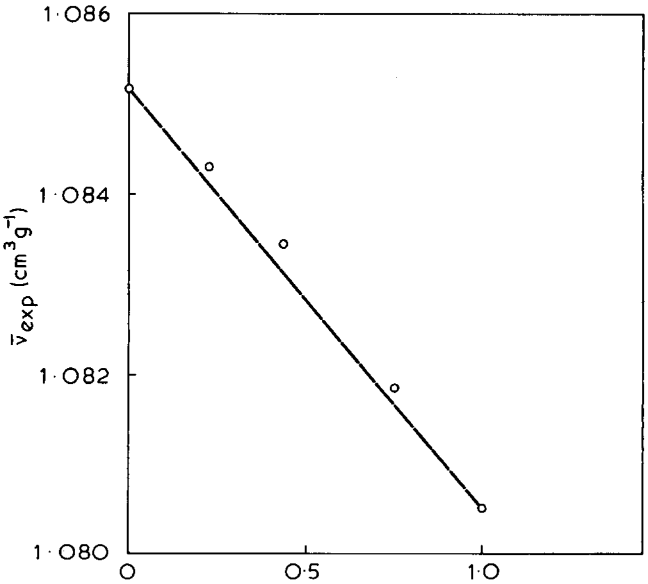

Figure 9 **Experimental specific volume, $\bar{v}_{\rm exp}$, *versus* st–PMAA weight fraction, x_w, for PVP/st–PMAA mixtures in DMF. [PVP 21] + [st–PMAA 125] = 4.73 wt %; temperature = 60°C**

DISCUSSION

Interpolymer complexes between PVP and atactic (at–)PMAA are known to possess equimolar composition in water[1,2,5,8] and in organic solvents like methanol, ethanol or dimethylformamide[1,3]. From the viscometric behaviour of PVP/st–PMAA mixtures in DMF (*Figure 2*) it may be concluded that an equimolar complex is formed in this case as well. The rather sharp minimum in η_{red} possibly reflects the specific character of the hydrogen bonding combined with special geometrical characteristics of the highly syndiotactic PMAA employed. According to Kabanov[17], the fulfilling of such conditions offers the possibility for a large number of complementary units to interact and to form very stable polymer complexes. From the time dependent behaviour of the reduced viscosity (*Figure 3*) it may be concluded that the complexation process is partially kinetically controlled but the position of the minimum in η_{red} does not shift (*Figure 2*). Ohno *et al.*[7] observed a similar phenomenon in the complexation behaviour of PMAA/poly(*N*,*N*-dimethyl, *N'*,*N'*,*N''*,*N''*-tetramethylenephosphoramide) in dimethylsulfoxide, by means of turbidity measurements.

From the unusual course of the Zimm plot obtained from laser light experiments we could derive an apparent molar mass of the complex of $\sim 10^7$. Bimendina *et al.*[5] also found a high value for PVP/at–PMAA complexes in water. Furthermore Ohno *et al.*[1] estimated a $\bar{M}_w$-value of $\sim 8.5 \times 10^6$ for the same system in DMF. No Zimm plot was given, however. The exact reason for the distortions in our Zimm plots is still unknown. In many instances deviations of the normal Rayleigh scattering behaviour have been mostly ascribed to the presence of dust, microgel particles or aggregates[18]. Their influence mostly finds expression in a rapid downward curvature at low angles and/or in a curvature in the concentration dependence. Neither of these effects was present in our case. Moreover, no large aggregates could have been formed, because filtration of the complex solution through a membrane filter with pores <200 nm, did not affect the intensity of scattered light. A possible influence of optical anisotropy of fluorescence in the complex solution is also not very likely.

According to Kerker[19], it is conceivable that the scattering particles reflect part of the incident light. Small spheres that show total reflection are known to cause an angular dependence of intensity which is the reverse of normal Rayleigh scattering. From the interferometric refractive index measurements of complex solutions however, we did not get the impression that reflection plays a role, because this would demand a high refractive index of a complex particle relative to that of the solvent. On the contrary, the refractive index increment of PVP/st–PMAA solutions, which amounts to just the mean value of that of the component polymers, lies in the normal range.

The most plausible explanation for the spurious Zimm plot resembles that of Ehrlich *et al.*[20] who found a similar angular dependence for a polyampholytic copolymer of methacrylic acid and 2-dimethylaminoethyl methacrylate in water at the isoelectric point. They observed an even more pronounced effect when small amounts of acid or base were added to the solution. The polyampholytic molecules behave like spherical particles which show some ordering in solution because of mutual repulsive forces. According to the hard sphere model of Fournet[21] such ordering can result in a so-called external or intermolecular interference with unusual scattering behaviour as a consequence. In the present system it is conceivable that the basic solvent DMF[22] causes ionization of some carboxylic groups[23] of uncomplexed st–PMAA chain parts, which are always present in stable complex particles to some extent[12]. The particles can therefore behave like globular polyelectrolytes, like the protein bovine serum albumin in water as reported by Doty *et al.*[24] The dramatic drop in viscosity as shown in *Figure 2* combined with the high molar mass of a complex particle signifies the compactness of the particles formed. The independence of η_{red} on shear rate and complex concentration (*Figure 4*) shows that the complex particles can be considered as hard spheres, obeying the Einstein equation $\eta = \eta_0(1 + 2.5\ \varphi)$, where φ represents the volume fraction occupied by the spheres. For PVP/at–PMAA complexes in water, Bimendina *et al.*[5] mentioned an analogous viscosity behaviour comparable with globular proteins in water. This was supported by sedimentation experiments in an ultracentrifuge. The globular structure can be deduced from the electron micrograph (*Figure 8*) showing round particles with a rather uniform diameter.

From φ in the Einstein equation and an estimated complex density of 1.3 g cm^{-3} from pycnometry, an amount of solvent within the coils of a complex of about 90% (v/v) has been calculated. An average of 10% (v/v) of pure polymer demonstrates the compact packing in comparison with unperturbed polymer coils in solution, which contain a maximum of about 3% (v/v) polymer segments in the centre while the average value over the whole chain is even less[25]. In other words, complex particles behave like polymers in a bad solvent below the θ-temperature, minimizing the interaction of the chains with solvent. On the contrary, mutual interaction between sections of the double chains of the polymer complex does occur and results in the formation of very compact particles as can be expected according to the calculations by El'Yashevich *et al.*[26] for interacting polymer systems in general.

The main interaction force between both component polymers is hydrogen bonding as could be concluded from Fourier transform infra-red spectroscopic studies. The carbonyl bond of PVP at 1676 cm^{-1} shifted to a lower frequency by 24 cm^{-1} on complexation, demonstrating the formation of hydrogen bonds[27]. On the other hand, the C=O stretching vibration of PMAA carboxyl groups shifted from 1700 to 1720 cm^{-1} which indicates that intra- or inter-molecular hydrogen bonds in the polyacid have been broken on complex formation.

The exact enthalpy change during the complexation process of PVP and st–PMAA is unknown but probably does not differ substantially from the value of -1 kJ/base mol for the complexation of PVP with at–PMAA in DMF, obtained from calorimetric studies by Abe *et al.*[9] This value is much lower than would be expected from the hydrogen bonding energy of low molar mass systems containing carboxyl groups[9,28]. The discrepancy may be explained by taking into account the breaking of polymer–solvent interactions in the overall process of complex formation. In the present case these interactions are very strong between the carboxyl groups of st–PMAA and DMF. In a 92/8 (v/v) DMF/NVP mixture preferential adsorption of DMF by st–PMAA has been established indeed[29,30]. Furthermore, ^{1}H n.m.r. studies of Ohno *et*

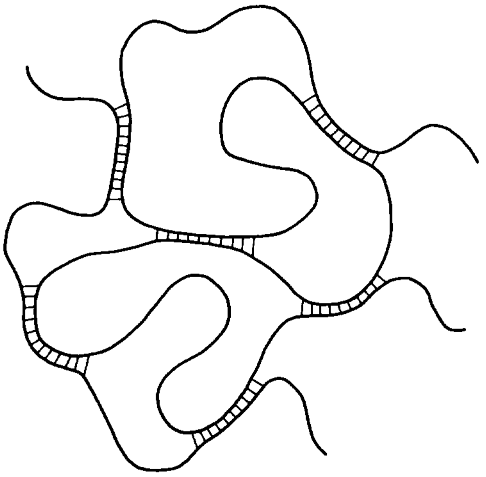

Figure 10 **Schematic drawing of part of a complex particle showing 'solvophobic interaction' (▥)**

al.[1] have shown that hydrogen bonding exists between the carboxyl proton of PMAA and the carbonyl group of DMF. Besides, some electrostatic interaction may exist because of proton transfer from some –COOH groups to DMF molecules[23].

From an enthalpic point of view PVP/st–PMAA complexation is not extraordinarily strong, but the cooperative character of the interaction between polymeric units can result in fairly stable complexes[10]. It might be expected that a temperature increase would involve complex destabilization because of hydrogen bond weakening[28]. At first sight, from an entropic point of view the same trend would be anticipated, because the formation of a rather stiff complex molecule from random coiled component polymers involves a negative conformational entropy factor, $\Delta S_{\mathrm{conf.}}$. Furthermore, the aforementioned formation of compact complex particles will additionally contribute to the negative $\Delta S_{\mathrm{conf.}}$ value, resulting in an overall negative entropy of complex formation. However, the temperature dependent viscometric and turbidimetric results (*Figures 5* and *6*), indicate that complex formation is contrarily favoured by an increase in temperature up to ~80°C, signifying an entropy driven complexation process. This overall entropy gain on complexation ($\Delta S_{\mathrm{compl.}} > 0$) stems from the liberation of DMF molecules which were originally presorbed by the st–PMAA chains. Liberation of the solvent molecules can be related to a positive desolvation entropy which more than compensates the negative $\Delta S_{\mathrm{conf.}}$.

The cooperative interaction between both polar component polymers results in the formation of apolar polymeric double chains which are thought to aggregate intra- and inter-molecularily in the polar medium DMF. From the high segmental density in complex particles it was concluded that interactions between sections of the double chains result in a compact structure. This is shown schematically in *Figure 10*, where double PVP/st–PMAA chains are presented as single lines.

A comparable process probably takes place during complex formation between PVP and at–PMAA[5,9,12] or methacrylic acid–maleic acid anhydride copolymer[31] in water where cooperative hydrogen bonding is followed by 'hydrophobic interactions' resulting in stable compact complex particles. It can be expected that in our non-aqueous system a process of 'solvophobic interaction' takes place between the α–CH_3 groups of complexed PMAA chains[1,32] and the hydrophobic parts of complexed PVP chains[33,34]. Although it is unlikely that DMF molecules possess any solvent structure around apolar complex molecules as is the case with water around biopolymers[35,36], it is conceivable that solvophobic interaction will be accompanied by a desolvation process. Packing of complex double chains can be so close that solvent molecules can no longer occupy the small cavities formed and are expelled as a consequence.

Including the liberation of solvent molecules from polymer chains on complexation, the overall desolvation leads to a positive entropy factor $\Delta S_{\mathrm{des.}}$ and to an increase in volume when PVP and st–PMAA form a complex (see Results). $\Delta S_{\mathrm{compl.}}$ can therefore be regarded as the sum of two different entropy terms:

$$\Delta S_{\mathrm{compl.}} = \Delta S_{\mathrm{des.}} + \Delta S_{\mathrm{conf.}}$$

At low temperatures $\Delta S_{\mathrm{des.}}$ dominates, especially the part which can be ascribed to desolvation of polymer chains.

On elevating the temperature, $\Delta S_{\mathrm{des.}}$ will be lowered because of an expected gradual decrease in preferential adsorption of DMF by the st–PMAA chains. This destabilizing factor starts to manifest itself above 80–90°C, the same transition region found by Ohno *et al.*[1] from transmittance measurements in the system PVP/at–PMAA in DMF.

In a previous paper[13], dealing with kinetic effects during the template polymerization of NVP along st–PMAA, it was postulated that desolvation of st–PMAA chains during the propagation step causes a larger overall activation entropy, $\Delta S^{\ddagger}$, than expected. Because of the similarity between *in situ* complex formation during the propagation of template associated PVP radicals and complex formation from ready-made polymers in solution, the postulation is supported by the positive value of $\Delta S_{\mathrm{compl.}}$, or $\Delta S_{\mathrm{des.}}$ in particular. However, we must realize that in the transition state during the propagation step DMF molecules will still be loosely bound to the PMAA units, so that the total entropy gain $\Delta S_{\mathrm{des.}}$ only partially contributes to $\Delta S^{\ddagger}$.

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