

Complexation

Influence of Concentration, Molecular Weight and Degree of Neutralization of Polyacrylic Acid on Interpolymer Complexes with Polyoxyethylene

I. Iliopoulos and R. Audebert

Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie Curie, Associé au CNRS n°278, E.S.P.C.I., 10, rue Vauquelin, F-75231 Paris Cedex 05, France

SUMMARY

Complexation of polyacrylic acid and polyoxyethylene in aqueous solution has been examined for various degrees of neutralization of the polyacid, different molecular weights and concentrations of the polymers. Potentiometric and visometric measurements show that the association of macromolecules is due to hydrogen bonding between sequences of vicinal carboxylic groups (minimum seven units) of the polyacid and polyether sequences. In several systems we observed a very high viscosity. This effect may be explained by a formation of highly branched structures, since the same polyacid molecule can be complexed with different polyether chains.

INTRODUCTION

It is well known that in aqueous solution polyacids, for instance poly(acrylic acid) (PAA), form complexes with polymers which act as hydrogen bond acceptors, like polyoxyethylene (PEO). The complexation results from cooperative interactions between long sequences of functional units, carboxylic and ether groups respectively. A 1/1 ratio in monomer units was reported (1-2). It has been shown that a minimum length of sequences is required for the complex formation (so called "minimum chain length" m.c.l.).

Most of the studies in aqueous solution have been devoted to interactions between homopolymers (3-6) and rarely to copolymers (7). In such systems the structure of the complexes formed should depend strongly on the regularity of the sites repetition along the chain. It is then interesting to investigate a simple model homopolymer/copolymer system. We have chosen PEO/PAA pair since PAA is easily transformed into a copolymer by neutralization and PEO has been extensively studied and its m.c.l. is well estimated (4,6).

In the present work the PEO/PAA system has been investigated by viscometry and potentiometry techniques. Several polymer samples with various molecular weights, concentrations and different degrees of neutralization of PAA were examined. It appears that even presence of a low content of carboxylate sites (inferior to 15%) in PAA chain is sufficient to destroy complexation. When complexation occurs the idea of global 1/1 stoichiometry cannot be maintained: a new structure of the complex is proposed in connection with experimental results.

EXPERIMENTAL

Materials

Origin, mode of purification and molecular weight of polymer species are

TABLE I

Sample	Molecular Weight	Purification	Origin
PEO - a	200	None	Fluka
PEO - b	750	"	Polysciences
PEO - c	1 500	"	Graham Cie
PEO - 2	21 000	Ultrafiltration :	Touzar & Mat.
PEO - 20	\bar{M}_w determined by	- Pellicon membrane	Aldrich
PEO - 90	viscosity measurement *	- Diaflo membrane	Aldrich
	450 000	- Diaflo membrane	
PAA - 5	100 000	"	Polysciences
PAA - 30	670 000	"	"
PAA - 25	800 000	"	"
PAA - a	800	Cation exchange	COATEX, France
PAA - b	1 800	resin "	"
PAA - c	4 000	"	"

* in water at 25°C according to ref.8.

** in 0.2 tetramethylammonium chlorid, the PAA was 20% neutralized by NaOH.

given in Table I. Water was purified by a Milli-Q system (Millipore). All other reagents were of analytical grade.

Apparatus

The elimination of simple electrolyte residues from polymers was performed by ultrafiltration in an "Amicon ultrafiltration cell -2000" using "Diaflo PM 10" or "Pellicon PSAC" membranes of 10 000 and 1 000 nominal molecular weight cut-off respectively.

A sofica 42 000 photogoniometer equipped with a laser source ($\lambda = 632.8\text{nm}$) was used for light scattering measurements and a Tacussel EPL 1 pH-meter for pH determinations.

The viscosity of solutions was measured in an Ubbelohde type viscometer and by a Low-Shear 30 apparatus (Contraves).

Experimental conditions

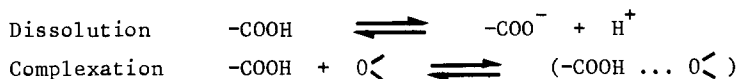
All the samples were prepared by mixing the solutions of the interacting components 24 hours before measurements, which were performed at 30°C.

For each series of experiments (pH or viscosity measurement) the PAA concentration was kept constant for each sample and only the unit molar ratio $r = \frac{[\text{PEO}]}{[\text{PAA}]}$ varies.

RESULTS

Potentiometry

Since in such system a double equilibrium process is involved :



the complexing reaction is accompanied by an increase of the pH of the solution.

Fig. 1 shows the typical shape of titration curves of PAA-30 with PEO-20 at various neutralization degrees, α , when the acid concentration, C , is 0.02 unit mol/l. No change of pH occurred for $\alpha = 0.15$. Similar curves were obtained with the other systems : PAA-30/PEO-2 ; PAA-5/PEO-2 ; PAA-5/PEO-20.

Calculation of the degree of complexation

The degree of complexation, θ , is the ratio of the concentration, C_c of carboxylic groups involved in a complex by the total concentration, C , of monomer units of PAA. $\theta = C_c/C$. θ is easily calculated from pH measurements since for a free acid in solution we have :

$$K_d = \frac{[\text{COO}^-][\text{H}^+]}{[\text{COOH}]} \quad [1]$$

We define d and d' by $[\text{H}^+] = Cd$ and $[\text{H}^+] = Cd'$, in absence or presence of PEO (calculated from pH values) respectively. If we take into account α , the degree of neutralization of PAA (calculated from the added quantity of NaOH:

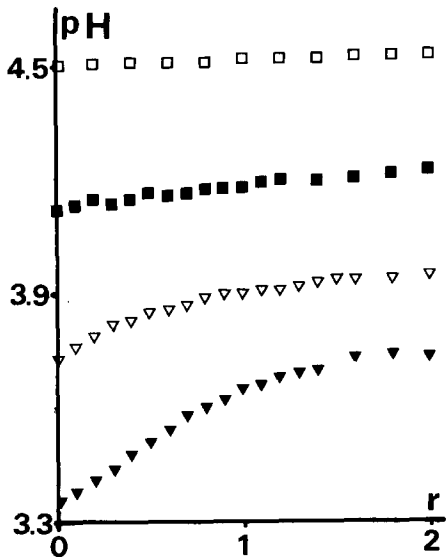


Fig. 1 : pH change versus unit molar ratio, r , for various degrees of neutralization of PAA, a . PAA-30/PEO-20 system. Concentration of polyacid, $C=0.02$ unit mol/l. $a=0$ (∇), $a=0.03$ (∇), $a=0.06$ (\blacksquare), $a=0.10$ (\square).

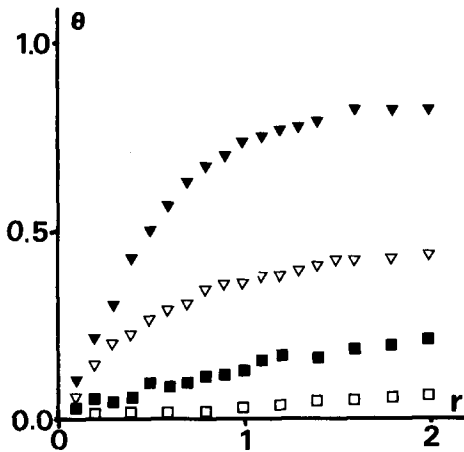


Fig. 2 : Degree of complexation, θ , vs. unit molar ratio, r , for PAA-30/PEO-20 system. Concentration and symbols as in Fig. 1.

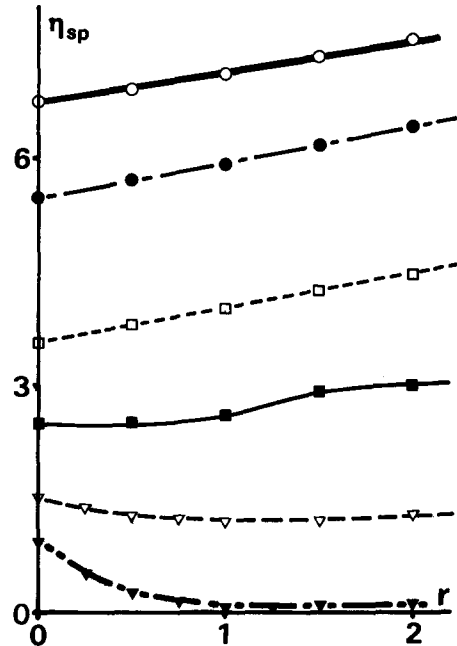


Fig. 3 : Specific viscosity of PAA-30/PEO-20 solutions, vs. unit molar ratio, r . $C=0.02$ unit mol/l. $a=0$ (∇), $a=0.03$ (∇), $a=0.06$ (\blacksquare), $a=0.10$ (\square), $a=0.15$ (\bullet), $a=0.20$ (\circ).

$[Na^+] = aC$) the relation (1) can be written, in absence of PEO :

$$K_d = \frac{C(a+d) \cdot Cd}{C - C(a+d)} = \frac{(a+d)d}{1 - (a+d)} C \quad [2]$$

and in presence of PEO :

$$K'_d = \frac{C(a+d')Cd'}{(C - Cc) - C(a+d')} = \frac{(a+d')d'}{[1 - (a+d')] - \theta} \quad [3]$$

If we suppose that K_d is a constant (that is true for a little variation of pH as K_d is an apparent constant) we obtain by combination of [2] and [3] :

$$\frac{(a+d)d}{1 - (a+d)} = \frac{(a+d')d'}{[1 - (a+d')] - \theta}$$

hence :

$$\theta = [1 - (a+d')] - [1 - (a+d)] \frac{(a+d')d'}{(a+d)d}$$

In figure 2, θ is plotted versus r for the same system as described in figure 1.

Viscosity

Figures 3 and 4 show the specific viscosity, η_{sp} , behaviour of PAA-30/PEO-20 system for two concentrations of PAA and various degrees of neutralization. The influence of the polymer molecular weight on η_{sp} can be estimated by comparison of fig 4 with fig. 5 relative to the couple PAA-25/PEO-90. In such a system the viscosity is very high if compared with the one of solutions of pure PEO or pure PAA in the same conditions. The gain of viscosity g , $g = (\eta_{sp}^{mixture}) / (\eta_{sp}^{PAA} + \eta_{sp}^{PEO})$ is given in figure 6.

DISCUSSION

Stoichiometry

If we consider fig. 1-5 where pH, degree of complexation and viscosity of solutions of mixed polymers are plotted versus r there is no discontinuity, especially for $r = 1$. For instance, even for $a = 0$ the pH increases markedly with the PEO content for $0 < r < 1$ and if the increase becomes lighter for $1 < r < 2$ it is not negligible (see fig. 1). This means, that the stoichiometry of the complex depends on the unit molar ratio, r , in agreement with Morawetz results (9) but in contradiction with conclusions reported by other authors, that PAA and PEO are present in the composition of the complexes in equimolar amounts independently of the initial value of r (5-6).

Moreover if partially neutralized PAA is used ($a = 0.03$ to 0.10) a regular evolution of pH curves occurs without any sign of fixed stoichiometry (see fig. 1 and 2) and no pH variation occurs for $a = 0.15$. Consequently little amounts of "defects" (acrylate groups) on PAA chains prevent complex formation.

Structure of the complex

When strong interactions between the two macromolecular chains are invol-

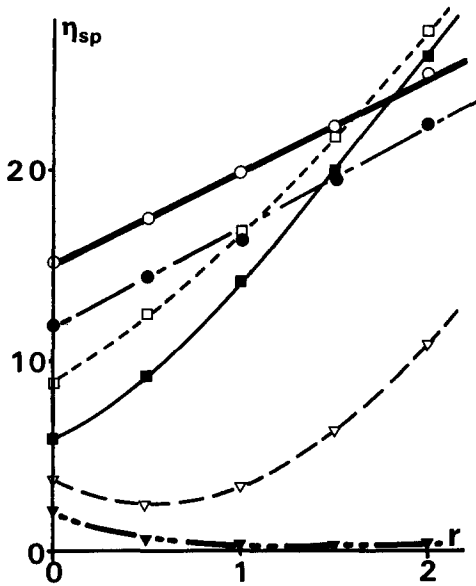


Fig. 4 : Specific viscosity of PAA-30/PEO-20 solutions vs. unit molar ratio. $C = 0.1$ unit mol/l. Symbols as in Fig. 3.

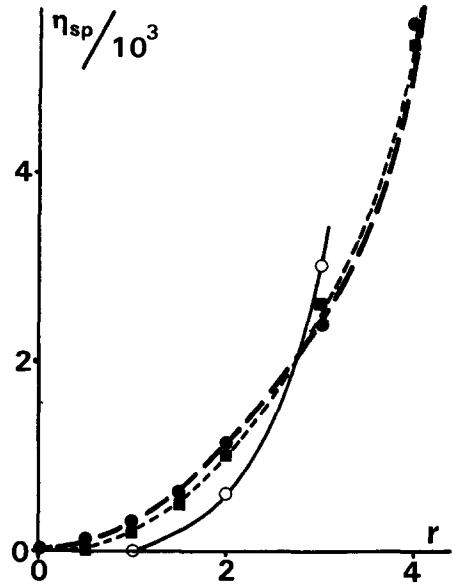


Fig. 5 : Specific viscosity of PAA-25/PEO-90 solutions, vs. unit molar ratio. $C = 0.1$ unit mol/l. $a = 0.03$ (○), $a = 0.04$ (■), $a = 0.05$ (●).

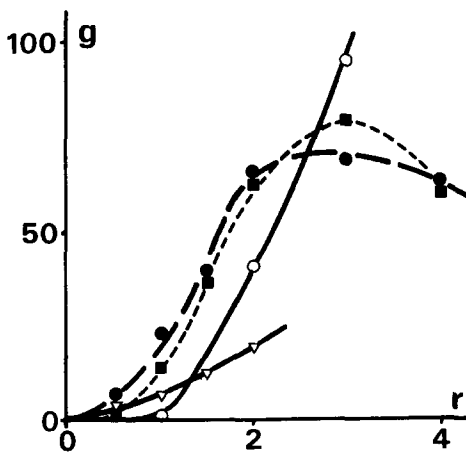


Fig. 6 : Gain of viscosity, g , versus unit molar ratio, r . Conditions as in fig. 5. $a=0.03$ (○), $a=0.04$ (■), $a=0.05$ (●), $a=0.10$ (▽).

ved a compact aggregate is expected to occur and consequently the solution viscosity decreases (3-4,6), an increase was reported only in special cases (10). Occasionally the complex may precipitate. In our case a decrease of viscosity is effectively observed for low carboxylate contents in the chains. But when the rate of free carboxylate groups on the PAA macromolecules reaches several percents the viscosity strongly increases (fig. 4-6). The viscosity increases with the concentration and the molecular weight of the polymers. Such a behaviour suggests that, when α increases the complex is less and less compact. The complexed sequences between two macromolecules are shorter and shorter. But then the various sequences of a given macromolecule can be probably complexed with sequences of several macromolecules of the complementary polymer. A highly branched structure (if not a tridimensional network) is formed. It disappears for sufficiently high value of α . For such values the mean length of sequences of carboxylic groups is very small and cannot lead to a complexation.

Minimal chain length for PAA complexation

It has been reported that for the cooperative effect involved in polyacid/PEO complex formation a minimum chain length, m.c.l., is required (4-6). With a high molecular weight PAA a chain length of PEO larger than about 200 monomer units is required for the complex formation (4,6). Our data on neutralization of PAA provide a useful method for estimation of m.c.l. : for a given PAA/PEO system and given conditions of concentration and stoichiometry (e.g. $C=0.02$ unit mol/l and $r=1$), θ and p ($p = a + d'$) can easily be determined for various degrees of neutralization by pH measurements. The mean length of COOH sequences in a PAA chain is $(\frac{1}{p} - 1)$. By plotting θ versus $1/p$ and extrapolating at $\theta = 0$ we find the minimum of $1/p$, $(1/p)_m$, and the m.c.l. of PAA. $(1/p)_m \approx 8$, consequently $(m.c.l.)_{PAA} \approx 7$. It appears that $(m.c.l.)_{PAA} \ll (m.c.l.)_{PEO}$. This marked difference may be explained by thermodynamic considerations.

If we consider two systems :

type 1 : long chains of PAA + oligomers of PEO ;

type 2 : long chains of PEO + oligomers of PAA ;

at the same concentration, unit molar ratio and degree of polymerization of oligomers.

The variation of enthalpy due to the formation of complexes is the same for the two systems. But the loss of entropy is larger for systems with very flexible oligomers (that is system 1) (11). Consequently the formation of complexes will be more difficult for systems of type 1 than for those of type 2.

Experimentally we tested 3 systems of type 1 : PAA-30 with respectively POE a, b, c (number average of monomer units 5, 17, 34), and 4 systems of type 2 : PEO-20 with respectively propionic acid, PAA a, b, c, (number average of monomer units 1, 11, 25, 56). The study was performed in 0.01M HCl to prevent acrylic group dissociation and under the conditions given for figure 7. As expected the viscosity of type 1 systems was unchanged (there is no complexation) ; for type 2 systems the viscosity of PEO-20 is not affected by propionic acid but progressively decreases by increasing the molecular weight of PAA oligomers (complex formation occurs).

In conclusion, the nature of interpolymer complexes is drastically changed by the introduction of some non complexing groups in the chains. The struc-

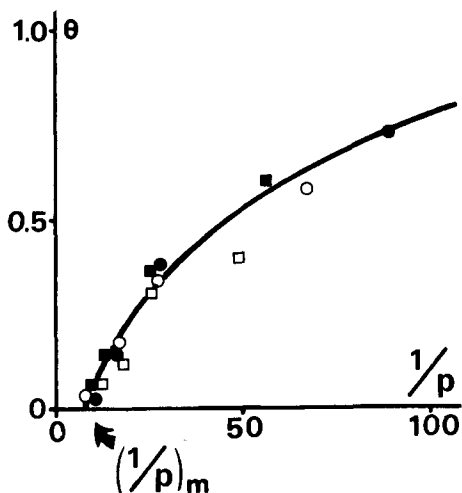


Fig. 7 : Dependence of the degree of complexation, θ , on $1/p$, for the systems : PAA-30/PEO-20 (●), PAA-5/PEO-20 (■), PAA-30/PEO-2 (○), PAA-5/PEO-2 (□). $C = 0.02$ unit mol/l. $r = 1$.

ture obtained depends on the rate of the non complexing sites and of the m.c.l.

ACKNOWLEDGEMENTS

The authors would like to thank the Soci t  d'Exploitation des Proc d s Coatex, for kindly supplying poly(acrylic acid) samples. One of them (I.I.) acknowledges with gratitude, financial support from Greek State Scholarships Foundation.

REFERENCES

1. E. TSUCHIDA and K. ABE, Adv. Polym. Sci., 45, 2 (1982).
2. E.A. BEKTUROV and L.A. RIMENDINA, Adv. Polym. Sci., 41, 99 (1981).
3. V.Y. BARANOVSKII, L.A. KAZARIN, A.A. LITMANOVICH, I.M. PAPISOV and V.A. KABANOV, Vysokomol. Soyed., A24, 1480 (1982).
4. T. IKAWA, K. ABE, K. HONDA and E. TSUCHIDA, J. Polym. Sci., Polym. Chem. Ed., 13, 1505 (1975).
5. Y. OSADA, J. Polym. Sci., Polym. Chem. Ed., 17, 3485 (1979).
6. A.D. ANTIPINA, V.Y. BARANOVSKII, I.M. PAPISOV and V.A. KABANOV, Vysokomol. Soyed., A14, 941 (1972).
7. L.A. BIMENDINA and A.A. KURMANBAEVA, Polym. Bull., 11, 557 (1984).
8. W. RING, H.J. CANTOW and W. HALTRUP, Eur. Polym. J., 2, 151 (1966).
9. H.L. CHEN and H. MORAWETZ, Eur. Polym. J., 19, 923 (1983).
10. E. TSUCHIDA, Y. OSADA and K. ABE, J. Polym. Sci., Polym. Chem. Ed., 14, 767 (1976).
11. Y.V. ANUFRIEVA, Y.Y. GOTLIB, M.G. KRATOVYAK and S.S. SKOROKHODOV, Vysokomol. Soyed., A14, 1430 (1972).

Accepted January 23, 1985