

## Gels of amphiphilic polyelectrolyte derivatives of poly(vinyl benzyl chloride)

Y. Rouault<sup>1,2,3</sup>, I. Iliopoulos<sup>1</sup>, R. Audebert<sup>1</sup>

<sup>1</sup> Laboratoire de Physico-Chimie Macromoléculaire, Université Pierre et Marie-Curie, CNRS URA-278, ESPI, 10 rue Vauquelin, F-75231 Paris cedex 05, France

<sup>2</sup> INRA, Unité de Science du Sol, Centre de Recherche de Versailles, Route de Saint-Cyr, F-78026 Versailles cedex, France

<sup>3</sup> Present and permanent address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

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### Summary

In this paper, we present some preliminary results on the phase behaviour of amphiphilic polyelectrolytes, derivatives of poly(vinyl benzyl chloride). The phase diagram of these copolymers contains, depending on the amount of amphiphilic units and on the polymer concentration, five different domains : an isotropic liquid and isotropic gel, a birefringent gel, a gel birefringent under stirring and a demixed gel.

### Introduction

Polyamphiphiles, or polymers containing among their constitutive units amphiphilic ones, sometimes differ markedly in their solubility or phase behaviour from their non polymerized counterparts. The comparison between the properties of free surfactants and surfactants attached to a polymer backbone is a half-century old field beginning with the pioneering work of Strauss(1). Strauss gave the name "polysoaps" to highly hydrophobic, but still soluble, polymers showing a compact conformation due to the intrachain hydrophobic interaction. The first studies were mainly based on the co-solubility of hydrophobic molecules (2,3). The phase diagram study of polyamphiphiles is more recent (4-6). For low molecular weight surfactants, lyotropic mesophases in water are always found when carefully searched for.

A common feature of the low molecular weight surfactants is their ability to form lyotropic mesophases in water at relatively high surfactant concentrations. However, polysoap behaviour does not imply the capability to form mesophases in water solution (4). During polymerization of surfactants in a mesophase, the mesophase can change to another one (7,8), or remains the same (9-12). The phase diagram is often different, sometimes richer with the appearance of mesophases absent in the non-polymerized system (5). Mesophases are generally reported for tail-end type geometries (i.e. the amphiphilic monomer is attached to the polymer backbone via the hydrophilic end) (4). Only a few cases of mesophases in water with soluble polysoaps of head-type geometries (i.e. the amphiphilic monomer is attached to the polymer backbone via the hydrophilic head) have been described (4,6,13,14).

We have recently developed a new family of head-type-geometry amphiphilic polymers (fig 1) based on poly(vinyl benzyl chloride) with a variable and well-controlled molar fraction X of dimethyldodecylammonium units (15). The second, non amphiphilic co-monomer, is hydrophobic which is a rather uncommon case for water soluble polysoaps (4,16,17).

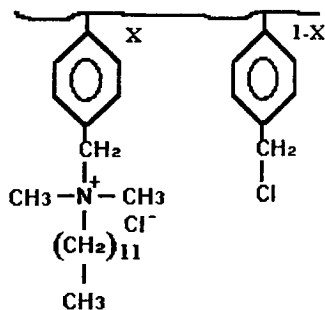


Fig. 1 Structure of the polyamphiphiles

As shown in this communication, our polyamphiphiles display an original phase behaviour including the formation of lyotropic liquid crystals in relatively dilute aqueous solution where the formation of liquid crystalline phases depends on the copolymer composition.

### Experimental

The synthesis and properties of the polysoaps are described in details elsewhere (15). Here, we just recall the main steps of the synthesis. Commercially available poly(vinyl benzyl chloride) is, in general, non-linear and cross-linked. We synthesized our own product using vinyl benzyl chloride (from Science Polymer Product) at 70°C in toluene with AIBN as initiator. <sup>1</sup>H-NMR and SEC measurements give  $M_n \sim 15000$  and  $M_w/M_n = 2$ . The polysoaps are easily synthesized at room temperature in chloroform by the reaction of a tertiary amine with a chlorobenzyl group. There is no need of an excess of amine if the molar fraction of dimethyldodecylammonium units per vinyl benzyl group X is lower than 90%.

The polymers obtained were dissolved in water and then freeze-dried. The <sup>1</sup>H-NMR measurements of the resulting material do not indicate the presence of either residual free dimethyldodecyl amine or of organic solvents used for the synthesis. The water solubility of these copolymers is limited to samples of intermediate composition ( $40 \leq X \leq 80$ ). The corresponding copolymers are named XD. Among these, we studied the phase diagrams of 52D, 68D and 80D for polymer concentrations,  $C_p$ , up to 10 wt %.

The phase diagrams were established by visual inspection of the samples with and without polarizers. The concentration and temperature were systematically varied from 0 to 10 wt % and from 10 to 90°C by increments of 0.5 wt % and 5°C, respectively. Near the phase boundaries, additional points have been taken so that the precision of the domain boundaries given on the figures is  $\pm 0.25$  wt % and  $\pm 2^\circ\text{C}$ . Viscosity measurements have been made at 22°C using a Couette geometry rheometer (Low-Shear-30, from Contraves).

### Sample preparation

A given amount of freeze-dried polymer was dissolved directly in an adequate amount of water in a screw-capped test tube equipped with a magnetic stirring bar, and continuously stirred for at least 24 hours before study. Checks were made to ensure that the glass tube was not birefringent. For this study, the glass tube is put in a thermostated bath and the bath is itself placed between cross polarizers.

Fig. 2 a) phase diagram of polymer 52D

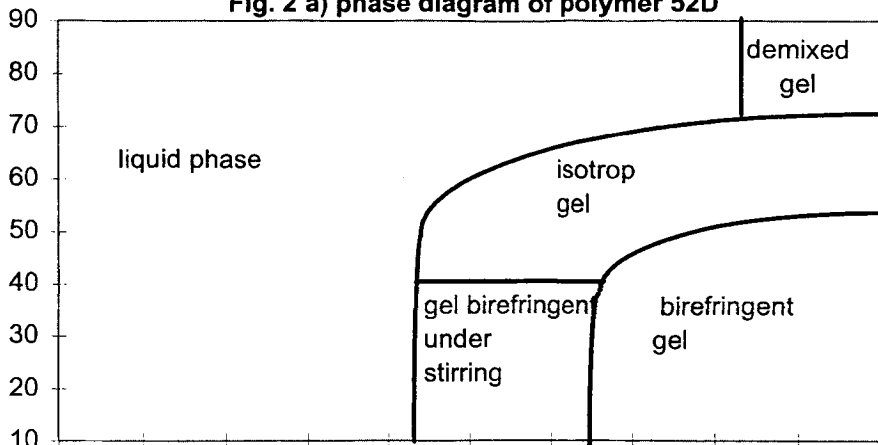


Fig. 2 b) phase diagram of polymer 68D

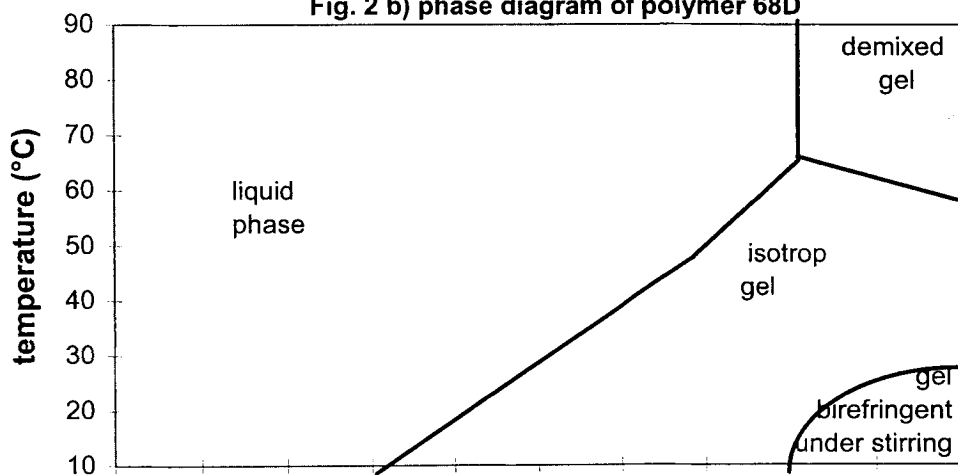
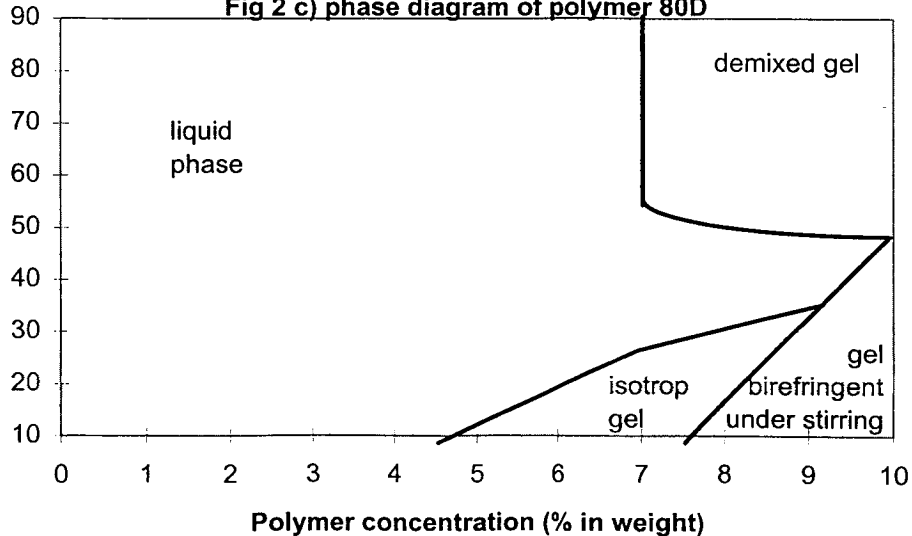


Fig 2 c) phase diagram of polymer 80D



## Results and discussion

The phase diagrams of the three polymers, namely 52D, 68D and 80D, are shown in fig 2a,2b and 2c respectively. The 52D sample shows the most complex phase diagram. For  $C_p \leq 5\%$  an isotropic liquid phase is observed at all temperatures. Below 40 °C, and for a concentration between 4 and 6.5 %, a gel birefringent under stirring is formed. When stirring is stopped, a few minutes are needed to recover the isotropic properties. By increasing the temperature, the gel is less and less birefringent under stirring, until it becomes an isotropic phase. By increasing the concentration above 6.5%, and for the same range of low temperatures, a birefringent phase is seen. Similarly to the previous case, an increase in temperature leads to the isotropic gel. Further increase in temperature leads either to an isotropic solution, for  $C_p < 8\%$ , or to a demixed gel, for  $C_p > 8\%$ .

The phase diagrams for the 68D and the 80D are qualitatively similar to the 52D, except for the birefringent phase without stirring which disappears. A general observation is that the phase boundaries move to higher  $C_p$  when  $X$  increases.

In some cases, after half an hour heating at high temperature ( $\sim 80$  °C), the samples do not appear, after recooling one hour at room temperature, to recover the same state as before the heating. At low polymer concentration, for which only a liquid phase is seen, an isotropic gel appears after heating and then cooling to room temperature. However, these samples retrieve the liquid phase after longer equilibration time at room temperature (between 2 days and one week). These phenomena are not surprising for polysoaps; cases of soluble polysoaps becoming insoluble after freeze drying or polysoaps insoluble at room temperature and becoming soluble at room temperature after heating, are reported (1,4,18).

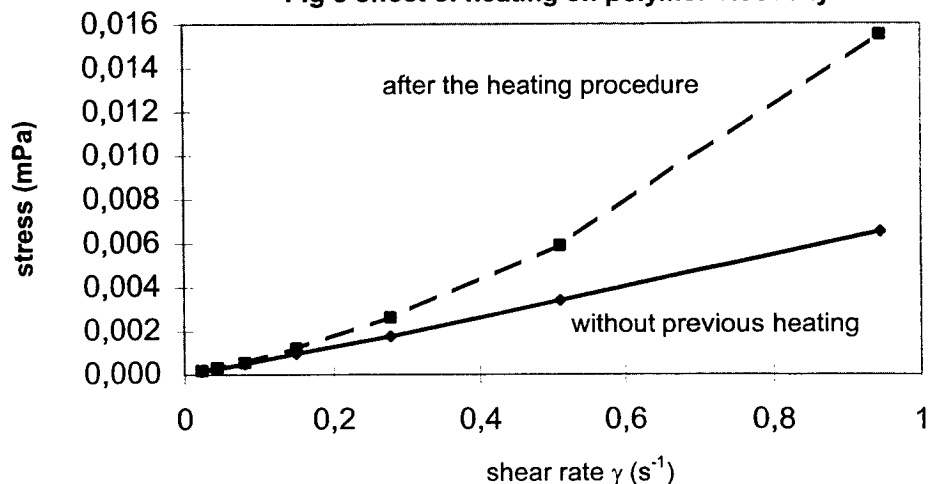
At higher concentrations, when a demixed gel is formed at high temperature, the behaviour is more complex. The demixed gel still remains present after cooling at room temperature, even after two months. However, the polymer in the demixed gel state, when put in an excess of water, is resolubilized. It is, however, not ruled out that hydrolysis of the chloromethyl group with water occurs at high temperatures (19), leading to a partial cross-linking of the system. We have left samples of a 10 wt % 80D solution for 3 hours at 80°C and solubilized the demixed gel phase obtained in an excess of water so that the final concentration of the solution was 3 wt %. The viscosity of this solution was compared to a reference 3 wt % 80D solution prepared at room temperature (fig.3). We have seen a slight increase in the viscosity after the heating process and have deduced that reticulation had taken place. However, we can postulate that the demixed gel is mainly of physical origin and that the cross-linking is only favored by the greater concentration of polymer in the rich polymer phase of the demixed gel. Indeed, the transition toward a demixed gel seems independent of the chemical composition of the polymer (i.e. the amount of unreacted chloromethyl groups in the polymer).

Nevertheless, the origin of the demixed gel should be clarified and future work involving hydrophobic co-monomers without the chloromethyl groups will be done.

The structures of the birefringent phases are not yet identified. Scattering techniques or cryo-TEM experiments are needed to determine them. In general, a birefringence without stirring implies an ordered structure.

Birefringence under stirring of isotropic phases is encountered when vesicles or cylindrical micelles are present (see for example (20) or (21)), and this is consistent with reports on head-geometry polyamphiphiles forming, under required conditions, cylindrical worm-like micelles (6,13,14,22-24). It is therefore quite possible that our copolymers form similar structures which presumably organize in a nematic phase at higher concentrations.

**Fig 3 effect of heating on polymer viscosity**



An interesting feature of the results is that the mesophases appear at a relatively low concentration (below 10% in weight), in comparison to other systems, and also with other polyamphiphiles based on quaternary ammonium derivatives (25) .

## References

1. U.P. Strauss, S.J. Assony, E.G. Jackson, L.H. Layton, *J. Pol. Sci.* 9:509 (1952)
2. U.P. Strauss, N.L. Gershfeld *J. Phys. Chem.* 58:747 (1954)
3. U.P. Strauss, N.L. Gershfeld, E. H. Crook, *J. Phys. Chem* 60:577 (1956)
4. A. Laschewsky, *Adv. Pol. Sci.* 124:1 (1995)
5. B. Luhmann, H. Finkelmann, G. Rehage, *Makromol. Chem.* 186:1059 (1985)
6. A. Mathis, A. Schmitt, A. Skoulios, R. Varoqui, *Eur. Pol. J.* 15:255 (1979)
7. S. Friberg, R. Thundathil, J.O. Stoffer, *Science*, 205:607 (1979)
8. R. Thundathil, J.O. Stoffer, S. Friberg, *J. Pol. Sci.: Pol. Chem* 18:2629 (1980)
9. F. Husson, J. Herz, V. Luzzati, *CRAS séance du 24 mai 1961* 3290
10. J. Herz, F. Husson, V. Luzzati *séance du 29 mai 1961* 3462
11. J. Herz, F. Reiss-Husson, P. Rempp, V. Luzzati, *J. Pol. Sci.:C* 4:1275
12. K. Naitoh, Y. Ishii, K. Tsujii, *J. Phys. Chem* 95:7915 (1991)
13. A. Schmitt, R. Varoqui, A. Skoulios, *C.R. Acad. Sci. C* 268:1469 (1969)
14. A. Mathis, A. Skoulios, R. Varoqui, A. Schmitt, *Eur. Pol. J.* 10:1011 (1974)
15. To be published
16. K. Nagai, I. Fuji, N. Kuramoto, *Polymer*, 33:3060 (1992)
17. K. Nagai, *Trends in Polym. Sci.* 4:122 (1996)
18. D. Cochlin PhD Thesis Strasbourg I (1992)
19. B. Verrier-Charleux, C. Graillat, Y. Chevalier, C. Pichot, A. Revillon, *Colloid Polym. Sci.* 269:398(1991)

20. M.J. Greenhill-Hooper, T.P. O'Sullivan, P.A. Wheeler *J. Colloid and Interface Sci.* 124:77 (1988)
21. H. Hoffman, U. Munkert, C. Thunig, M. Valiente, *J. Colloid and Interface Sci.* 163:217 (1994)
22. L.-B. Shih, D. H. Mauer, C. J. Verbrugge, C. F. Wu, S. L. Chang, S. H. Chen *Macromolecules* 21:3235(1988)
23. L.-B. Shih, E. Y. Sheu, S. H. Chen, *Macromolecules* 21:1387(1988)
24. D. Cochin, F. Candau, R. Zana, Y. Talmon *Macromolecules* 25:4220 (1992)
25. S.K. Abid, D.C. Sherrington *Eur. Polym. J.* 29:153 (1993)