'Gel collapse' in the saponified starch-g-polyacrylonitrile/water–alcohol system*

Cenita Rodehed and Bengt Rånby
Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

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A sample of starch-g-polyacrylonitrile (grafting ratio 82%) has been prepared at 303 K using the Mn^{3+} complex ion as initiator in aqueous acid solution with gelatinized starch as substrate. Subsequent alkaline hydrolysis converts the nitrile groups to carboxamide ($\sim$30%) and sodium carboxylate ($\sim$70%) groups. The swelling of the copolymer formed which retains about 700 g water per g of dry copolymer, has been studied in alcohol/water mixtures of increasing alcohol content at 294, 304 and 314 K. The liquid retention vs. alcohol concentration indicates one minor transition for ethanol/water mixtures and possibly two small transitions for methanol/water mixtures. The main transition for both alcohol/water mixtures is a collapse of the gel at 50–60 volume% ethanol and 60–70 volume% methanol, respectively. Increasing the temperature from 294 to 314 K increases the liquid retention and moves the transitions to higher alcohol concentrations by 5–10 volume%. When the starch copolymer is hydrolysed in dilute mineral acid to remove the starch moiety, the retention values increase by a factor of approximately 3 for both pure water and alcohol/water mixtures. The retention vs. methanol concentration curves show three transitions which are similar to those of the starch copolymer before acid hydrolysis. A tentative interpretation of the transitions is proposed and discussed.

(Keywords: saponified starch-g-polyacrylonitrile; liquid retention; alcohol–water retention; gel collapse; gel transitions)

INTRODUCTION

Renewed interest in the gel transitions has developed since Tanaka[1,2] reported the collapse of saponified polyacrylamide gels caused by changing temperature and acetone concentration in the acetone–water gel fluid mixture. Phase transitions in crosslinked polyacrylamide gels were later studied by Stejskal *et al.*[3], Janas *et al.*[4] and Ilavsky[5]. Small changes in an external parameter such as temperature or composition of solvent, may result in gel collapse. Ionization of the polymer network is an important parameter in the phase transition. A non-ionized polyacrylamide gel shows continuous transitions when external parameters are changed. If a small amount of the amide groups are hydrolysed to ionizable carboxyl groups, a discrete reversible gel collapse is observed as a result of infinitesimal changes in external parameters. Both increasing content of charged groups[5] and decreasing network density[6] are found to enhance the phase transition and affect the critical value of the interaction parameter at which the collapse takes place. Ilavsky *et al.*[7] also reported how the amount of diluent in the network formation can influence the phase transition.

Recently a highly water absorbing polymer of saponified starch-g-polyacrylonitrile has been developed in this laboratory using a Mn^{3+} pyrophosphate complex as initiator for the grafting reaction[8–11]. The molecular structure and properties[8] and morphology[9] of this product have been studied. The absorption of water vapour[10], the retention of aqueous solutions[10] and the water structure[11] in this hydrophilic polymer have also been studied. During the alkaline hydrolysis of starch grafted with polyacrylonitrile, all nitrile groups detectable by infra-red absorption are destroyed and converted to amide and carboxyl groups. Rogers[12] has reported a maximum conversion of 70% of nitrile to carboxyl groups. The remaining 30% are amide groups. The incomplete hydrolysis is interpreted as being related to steric and polar factors, e.g. hydrogen bonding of neighbouring amide and carboxyl groups. Weaver *et al.*[13] suggest that condensation may also occur between carboxyl and amide groups to form imide structures.

This paper is a study of the effect of solvent compositions and temperature on the retention of water/alcohol mixtures in saponified starch-g-polyacrylonitrile and in the saponified branches after removal of the starch component.

EXPERIMENTAL

Sample preparation

Starch-g-polyacrylonitrile was prepared as previously described[8], with initially equal amounts of gelatinized starch and acrylonitrile, using the Mn^{3+} pyrophosphate complex as initiator. The grafting ratio [= (polymer in grafts/weight of substrate) × 100] of the graft copolymer was 82%. The molecular weight of the grafted polyacrylonitrile chains, determined from viscosity measurements in DMF after acid hydrolysis of the grafted polymer, was calculated to be 630 000 from the relation[15]: $[\eta] = 3.92 \times 10^{-4} \times \bar{M}_n^{0.75}$ (c in g/100 ml). The alkaline hydrolysis was carried out for approximately 2 h at 363 K in 1% aqueous sodium hydroxide. A deep red colour develops during the hydrolysis due to intermediate formation of naphthyridine ring structures from adjacent nitrile groups[14]. The intermediate rings are subsequently hydrolysed with a resulting colour change from red to

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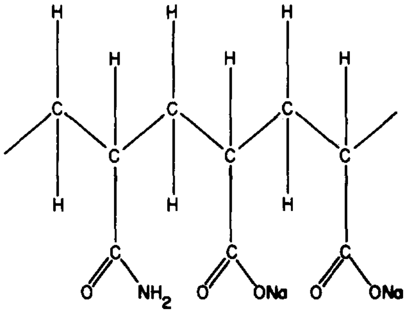
light yellow. This sharp colour change was used as an indication to halt the hydrolysis. The product was recovered by precipitation in methanol, washed to neutrality and dried to constant weight. Infra-red absorption analysis showed no nitrile functionality after the saponification reaction. Samples from the same batch were used for all experiments. Grafted saponified polyacrylonitrile chains were separated from the starch backbone by acid hydrolysis. The starch moiety is therefore hydrolysed to glucose and other water soluble carbohydrate fragments. The remaining synthetic branches are protonated during the acid hydrolysis and were converted back to sodium carboxylate groups with aqueous sodium hydroxide solution.

Retention measurements

The liquid retention of the gels as a function of solvent composition was studied for water/alcohol mixtures (methanol or ethanol) at different temperatures. A weighed sample of dry polymer was immersed in a known amount (in g) of water/alcohol mixture in a test tube. After 30 min at constant temperatures (294 K, 304 K and 314 K, respectively), the slurry was filtered and the amount of retained liquid (difference in weight between initial liquid added and final filtrate) calculated. The liquid retention value (*LRV*) was calculated in grams per gram of dry sample charged. Refractive index measurements were used to check that the alcohol content in the solutions was the same before and after swelling (accuracy is no better than ±3%).

RESULTS AND DISCUSSION

The absorbent which was developed in this laboratory[8–11], has functional groups similar to those in the crosslinked gels studied by Tanaka[1,2], Stejskal *et al.*[3], Janas *et al.*[4] and Ilavsky[5]. Saponified starch-g-polyacrylonitrile has a starch backbone with side chains that carry sodium carboxylate and carboxamide as functional groups.



Some crosslinks may form during the graft copolymerization. Incompletely hydrolysed structures probably also give rise to a few crosslinking points between adjacent polyacrylonitrile chains[8]. Hydrogen bonds may also form between carboxylate or carboxamide groups on side chains and hydroxyl groups on the starch backbone, which would limit the swelling of the polymer network[8].

Figure 1 shows the liquid retention (in grams of solvent per gram of dry sample) as a function of solvent composition for water/ethanol mixtures. The temperatures used (294 to 314 K) have no influence on the retention capacity for pure water. However, raising the temperature caused the retention of water/alcohol mixtures to increase considerably especially at higher alcohol concentrations (*Figure 1*). This is also found for the water/methanol system (*Figure 2*). Presentation of the retention data in *Figures 1* and *2*, leads to the impression of continuous transitions in these systems. If, however, the retention data are presented as retention ratios (retention of pure water/retention of different alcohol/water mixtures) comparable with the volume ratios used by Tanaka[1,2], a discrete transition (a gel collapse) is observed. This is shown in *Figure 3* for water/ethanol and water/methanol mixtures at 294 K. This method of data presentation does not show all information possible from the measurements.

Figure 3 shows a discrete gel collapse when the ethanol content exceeds 50 volume% and the methanol content exceeds 60 volume%. *Figure 1* shows two phase transitions for water/ethanol mixtures at 294 K, although the first transition occurring between 10 and 15 volume%, is a minor one. The first transition reduces the retention capacity from 700 to approximately 550 g of solvent per gram of dry sample, while the second transition is a reduction of the retention capacity from approximately 500 to 0, i.e. a collapse of the swollen gel. With water/methanol mixtures as swelling solvent, the first transition at 294 K is not as obvious as with water/ethanol mixtures and could possibly be divided into two minor transitions.

Figures 4–6 show comparisons of retention curves for ethanol/water and methanol/water mixtures at different temperatures. The first transition becomes more

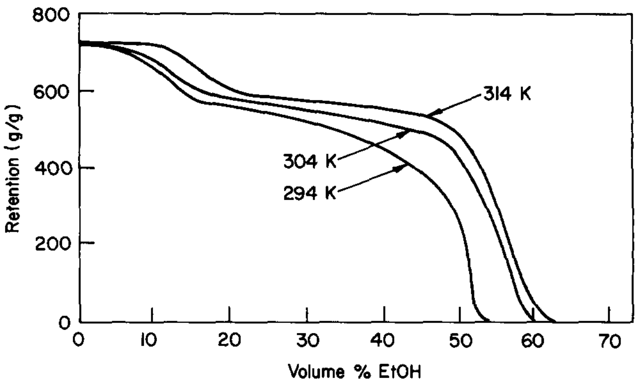


Figure 1 Liquid retention as a function of volume% ethanol at 294, 304 and 314 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio

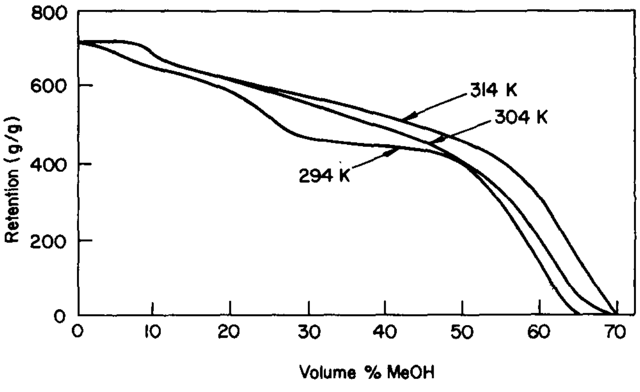


Figure 2 Liquid retention as a function of volume% methanol at 294, 304 and 314 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio

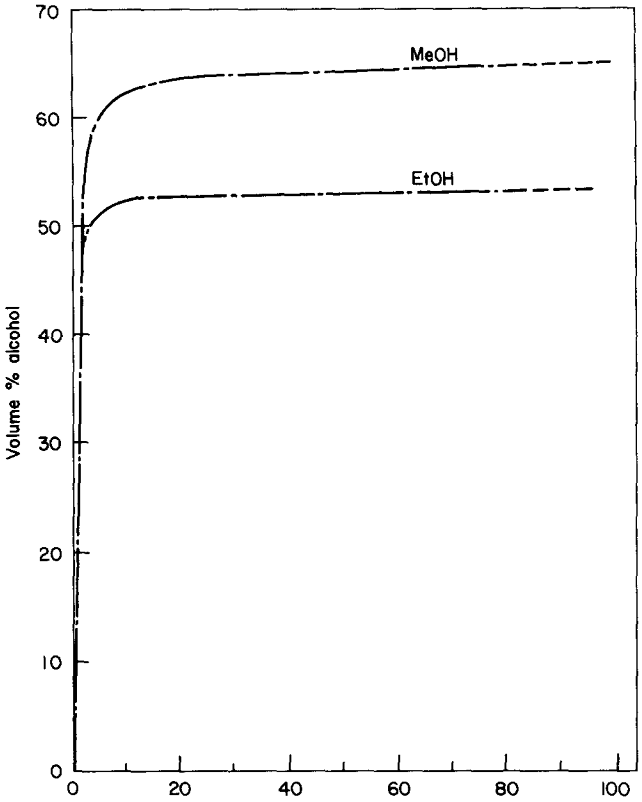


Figure 3 Volume% ethanol and volume% methanol, respectively, as a function of retention ratio at 294 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio

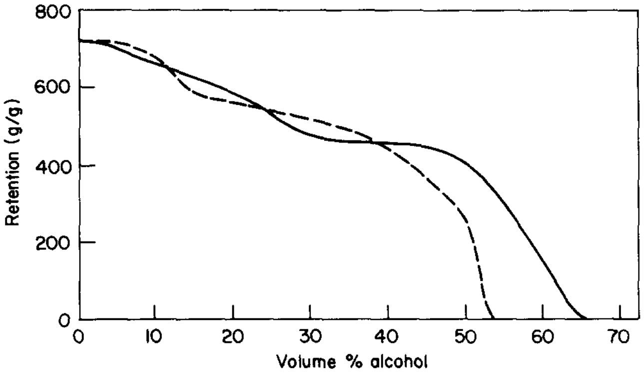


Figure 4 Liquid retention as a function of solvent composition at 294 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio (———) MeOH, (-----) EtOH

pronounced with increasing temperature for the methanol/water system. At 314 K the first transition in the ethanol/water system is larger and broader than that of the methanol/water system. The magnitude of the large transition (the discrete collapse of the gel) is almost the same for the two solvent systems but occurs at approximately 10 volume% higher alcohol concentration for the methanol/water system.

To study the dependence of the gel transitions on the gelatinized starch backbone, acid hydrolysis of saponified starch-g-polyacrylonitrile for starch removal was carried out, as described in the experimental section. The synthetic branches have liquid retention curves in alcohol/water mixtures that are similar to those of the saponified starch copolymer. This is shown in *Figure 7* for the methanol/water system at two temperatures. However, the retention capacity is increased by a factor of approximately 3. This is due partly to the removal of the starch moiety which has a much lower retention capacity. In addition, hydrolysis of the starch backbone decreases the number of crosslinks which allows a further expansion of the polymer network and gives higher retention values[8]. Three transitions are indicated, both at 294 and 314 K: the first (a minor transition) at about 5 volume%, the second at 25–30 volume% and the third (the gel collapse) at 60–70 volume% methanol. At higher temperatures, the retention is higher and the transitions are moved to higher alcohol concentrations.

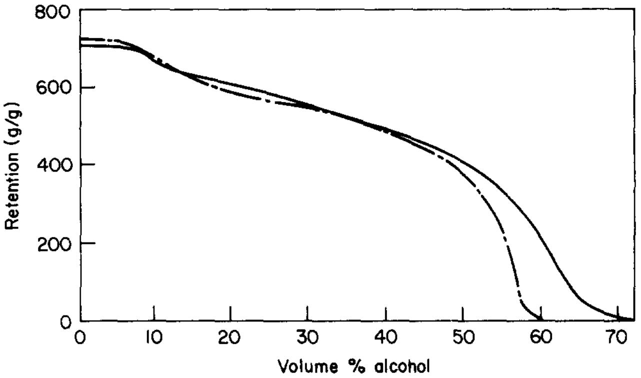


Figure 5 Liquid retention as a function of solvent composition at 304 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio (———) MeOH, (-·-) EtOH

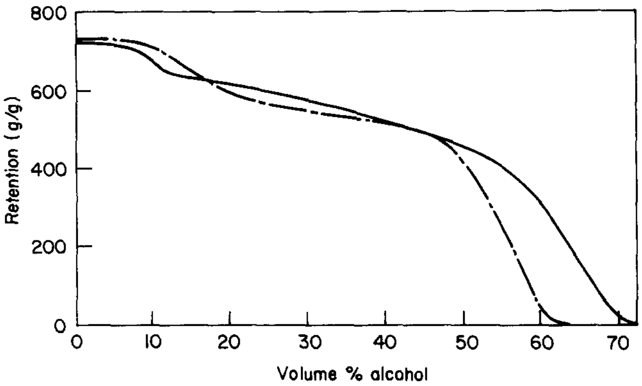


Figure 6 Liquid retention as a function of solvent composition at 314 K for saponified starch-g-polyacrylonitrile with 82% grafting ratio (———) MeOH, (-·-) EtOH

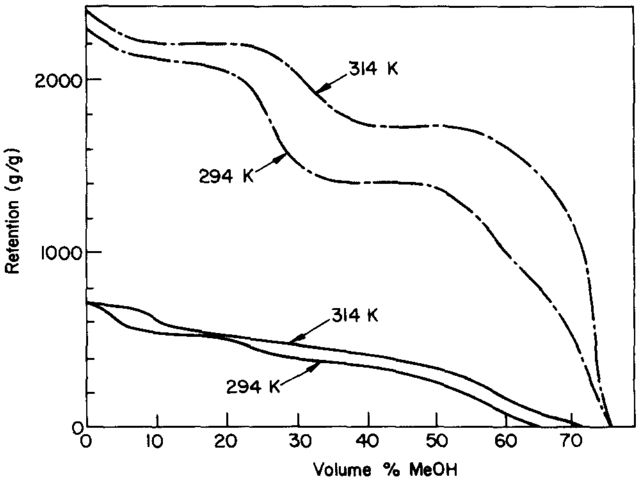


Figure 7 Liquid retention as a function of volume% methanol at 294 and 314 K for saponified starch-g-polyacrylonitrile and the synthetic branches (after removal of the starch component), respectively (———) before acid hydrolysis, (-·-) after acid hydrolysis

To interpret the gel transitions of the saponified starch-g-polyacrylonitrile gel on a molecular basis, more experimental data is required. By comparison of the results obtained in this work with those of the differential scanning calorimetric studies of the same product[11], a tentative interpretation can be made. The water absorbed by saponified starch-g-polyacrylonitrile can be described as being of three types; bound water, crystallizable water weakly interacting with the polymer and free bulk crystallizable water. Assuming that a water/alcohol mixture interacts with the polymer in the same way as pure water, the first transition at low alcohol concentration could be due to forcing the 'free' liquid out of the polymer network. This agrees with the observation that the first transition is larger and more pronounced when the starch backbone is removed and leaves a more expanded polymer network. The second discrete transition (at 50–70 volume% alcohol) is also affected by the starch moiety and is presumably of the same type as the gel collapse described by Tanaka[1,2]. If this transition is due to an interaction between the liquid and the ionizable groups on the polymer, the magnitude of the transition would increase when the starch backbone is removed. This releases restrictions to swelling and eliminates hydrogen bonds between carboxylate and carboxamide groups on the branches and hydroxyl groups on the starch moiety. This can also be seen when the retention curves in *Figures 2* and *7* are compared. This leads to the following tentative proposals: The first transition is interpreted as being due to polymer–polymer affinity causing the free liquid in the gel to be forced out and is an effect of increased alcohol content. The second (major) transition is probably due to interaction between polar groups in the liquid and ionizable groups on the polymer. This would also explain why the ethanol/water gel system collapses at a lower alcohol content than the methanol/water gel system as methanol has a higher polarity than ethanol. The collapse of the gel is a result of the total depletion of water due to competitive extraction of water from the solvated polymer network.

ACKNOWLEDGEMENT

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