

Synthesis and rheological behaviour of new hydrophobically modified hydrogels

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We report the synthesis and characterization of a family of hydrophobically modified hydrogels designed to have an improved fracture resistance. A backbone of poly(acrylic acid) (PAA) was functionalized with double bonds and hydrophobic groups. The functionalized PAA was then crosslinked with a dithiol. The chemical structure of the gels was characterized with a combination of NMR, titration methods and rheological techniques. The crosslinked structure of the hydrogel was found to be dependent on the polymer concentration only, while the dissipative properties of the gel increased strongly at all frequencies, with the introduction of hydrophobic groups which formed reversible associations. We expect these viscoelastic hydrogels to display dramatically different properties from the unmodified hydrogels when stretched and fractured.

Introduction

While the structure and the swelling properties of hydrogels have been the focus of considerable scientific interest in the past decades, their mechanical properties have been less investigated and are less well understood despite a clear technological relevance. The main goal of our study is to understand the role played by temporary cross-links in controlling the fracture mechanism of hydrogels. For this purpose we have prepared novel and original hydrophobically modified hydrogels by chemical crosslinking, in aqueous media, a physical network formed by poly(sodium acrylate) chains grafted with alkyl groups. The synthesis, the primary structure and the rheological behaviour of these systems are reported in this presentation.

Experimental Part.

Modification of PAA with hydrophobic side groups and double bonds.

PAA chains were initially treated with allylamine in order to introduce double bonds along the macromolecular backbone while some of them were modified afterwards with different proportions of short hydrophobic chains. Both modifications were carried out by grafting amino-terminated molecules onto carboxylic acid functions of PAA using carbodiimide chemistry¹.

Three different polymers were synthesized. The mole % of double bonds was fixed at 10% while the mole fraction of dodecyl chains was respectively 0%, 3% and 5%. These polymers are referred to as: PAA10db, PAA3C12 and PAA5C12.

Preparation of the hydrogels.

Thiols, which can easily produce free radicals through a redox mechanism with potassium peroxodisulfate, are very good candidates to react with double bonds². In the present case, we used a difunctional thiol,

dithioerythritol ($C_4H_{10}O_2S_2$), in order to crosslink the double bonds of the PAA precursors.

Results and Discussion

Characterization of the modified PAA.

The structure of the gel precursors: PAA10db, PAA3C12 and PAA5C12 was characterized by ¹H NMR in D₂O. The results clearly indicate a quantitative grafting of all amino-terminated molecules.

Regimes of concentration.

According to the Fuoss law, the viscosity of low ionic strength polyelectrolyte solutions in the dilute and unentangled semidilute regimes should scale as $C^{1/2}$ while in the entangled semidilute regime, Dobrynin et al.³ predicted a $C^{3/2}$ dependence for the viscosity. This behaviour is clearly illustrated in figure 1 with the solutions of the hydrophilic PAA10db precursor.

Figure 1.

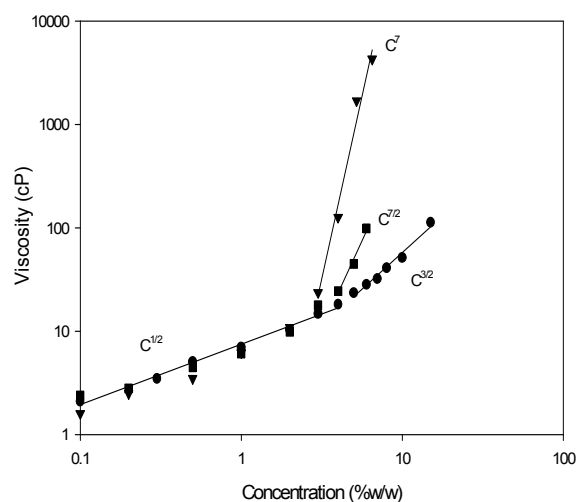


Fig. 1: Viscosity (cP) against concentration (% w/ w) for PAA10db (●), PAA3C12 (■) and PAA5C12 (▼)

The same holds below 2% w/w for solutions of PAAxC12, even if the viscosities remain slightly lower

than those of the PAA10db. In this concentration regime, hydrophobic associations mainly occur intramolecularly and tend to reduce the hydrodynamic radius of the macromolecules⁴. On the contrary, above 3% w/w for the PAA5C12 and above 4% w/w for the PAA3C12, the viscosity of hydrophobically modified polymers increases sharply with higher scaling coefficients due to the increasing influence of inter-chain associations.

Molecular characterization of chemical hydrogels.

Although ideally each dithiol can form an intermolecular bridge between two different PAA chains, there are other possibilities which will affect the architecture and the properties of the network, as shown in Figure 2.

In order to estimate the yield of the cross-linking reaction, we used a series of titration methods with I₂ and Fe³⁺. We conclude that, independently from concentration and presence of hydrophobic groups in the sample, 40% of the thiol functions are creating dangling thiols (case 2 in figure 2), while 60% are involved in inter- or intra-molecular cross-linking (case 1 and 3). The case 4 is mainly inexistent.

Figure 2.

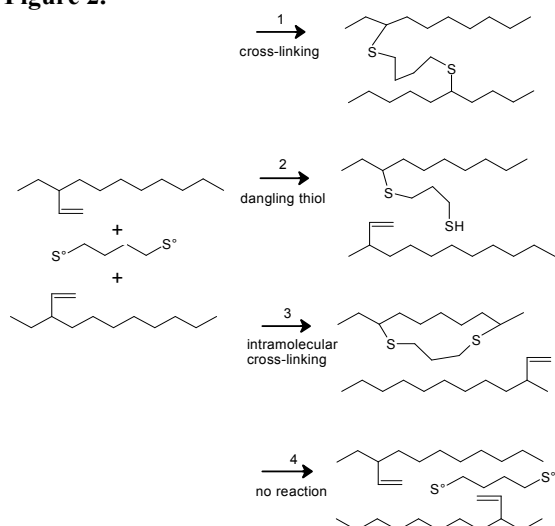


Fig.2: Schematic representation of the competition between all possible reactions during gelation. Reaction 1 only allows gelation.

Using the statistical theory of rubber elasticity, we showed, by comparison between rheological measurements and titration, that the ratio between cases 1 and 3 is strongly concentration dependant, but is only about one to six for a 10% w/w hydrogel. These results were confirmed by micro-DSC measurements.

Kinetics of gelation.

As shown in figure 3, if the gel time is defined as the moment when $G' = G''$, it is clearly modified by the presence of alkyl groups which render the material more solid-like much sooner. However, the rheological measurements also show that there is a second

inflexion for the hydrophobically modified hydrogels, both for G' and G'' . This second transition occurs at the same time as the “gelation” for the unmodified hydrogels (t_2 on Figure3) and can be correlated to the chemical gelation process which is not modified by the presence of hydrophobic groups. This was verified by micro-DSC measurements. Concerning the first transition (t_1), we conclude that this behaviour is only due to an increased viscosity of the solution due to hydrophobic groups.

The final moduli of our hydrogels were measured once the plateau value was reached, after completion of the reaction (see figure 3). The remarkable result is that the final storage modulus G' of the gel was found to be independent of the presence or absence of hydrophobic groups. On the other hand the loss modulus G'' dramatically increased with increasing hydrophobic groups concentration suggesting the formation of non permanent associations introducing a dissipative mechanism independent of the solvent viscosity.

Figure 3.

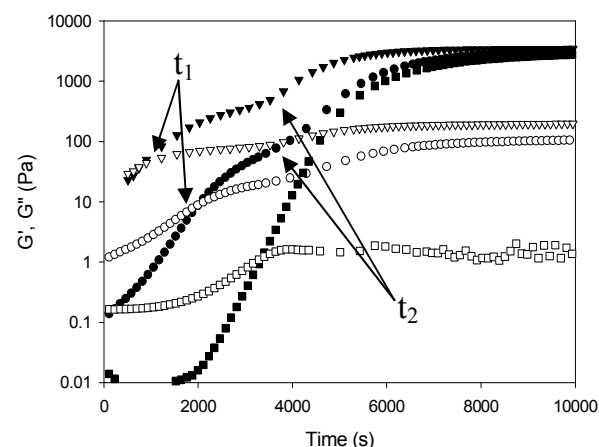


Fig.3: Comparison of gelation for PAA10db (■ for G' , □ for G''), PAA3C12 (● and ○) and PAA5C12 (▼ and ○) at 6% w/w.

Conclusion.

We synthesized and characterised new hydrophobically modified hydrogels, displaying the elastic behaviour expected from a classical gel but with a much larger loss modulus. We expect these gels to display significantly different properties in large strain and fracture and some preliminary results will be presented at the conference.

References

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