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Synthesis and Viscoelastic Properties of Hydrophobically Modified Hydrogels

Guillaume Miquelard-Garnier, Costantino Creton, Dominique Hourdet**

Summary: 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.

Keywords: amphiphilic networks; hydrogels; synthesis; viscoelasticity

Introduction

While the structure, swelling properties and elastic modulus of hydrogels[1–6] have been the focus of considerable scientific interest in the past decades, their mechanical properties at large strain and their fracture properties[7–11] 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 physical interactions acting as reversible cross-links in controlling the fracture mechanism of hydrogels. For this purpose we have prepared original hydrophobically modified hydrogels (also called amphiphilic polymer networks[12–13]) by chemically crosslinking, in aqueous media, a solution of poly(sodium acrylate) (PAA) chains grafted with alkyl groups. The synthesis, the primary structure and the rheological behavior of these systems are reported in this article.

Modification of PAA with Hydrophobic Side Groups and Double Bonds

All PAA chains were initially reacted with allylamine in order to introduce double bonds along the macromolecular backbone. These double bonds will then be the sites of chemical crosslinks. Some of the functionalized polymers were subsequently modified with different proportions of short hydrophobic chains along the backbone. Both modifications were carried out by grafting amino-terminated molecules onto carboxylic acid functions of PAA using carbodiimide chemistry.[14]

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.

The structures of PAA10db, PAA3C12 and PAA5C12 were characterized by

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Physico-Chimie des Polymères et des Milieux Dispersés, UMR 7615, UPMC-CNRS-ESPCI, 10 rue Vauquelin, 75005 Paris, France
Fax +33 (0)1 40 79 46 86
E-mail: costantino.creton@espci.fr;
dominique.hourdet@espci.fr

Table 1.
Nomenclature and composition of modified PAA.

Polymers	Grafting ratio (mol %)			Grafting yield (%)		Reaction yield (%)	M_{eq} (kg/mol)
	DB	C12	$N_{C12/chain}$	DB	C12		
PAA							0.094
PAA10db	10	0	0	100	100	80	0.0957
PAA3C12	10	3	11	100	100	50	0.1
PAA5C12	10	5	19	100	100	50	0.1027

^{1}H NMR in D_2O using an Avance Brücker Spectometer at 300 MHz. The results clearly indicated a quantitative grafting of all amino-terminated molecules.

Polymer Solutions

Steady state viscosity of aqueous solutions of network precursors was measured at very low shear rate in the Newtonian domain with a Contraves LS 30 low shear rheometer.

According to the Fuoss law,[15] 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.[15] 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. This gives a rough estimate of the beginning of the entangled regime, which occurs around $C_e = 5–6\%$.

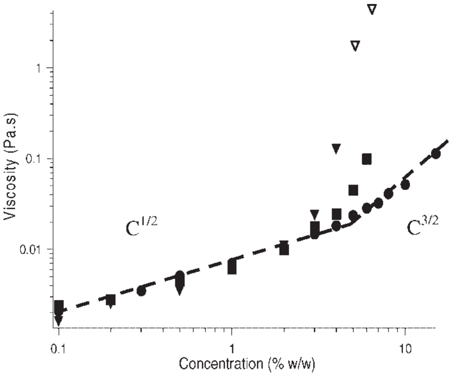

Figure 1.
Newtonian viscosity (Pa.s) against concentration (% w/w) for PAA10db (●), PAA3C12 (■) and PAA5C12 (▼). PAA5C12 viscosity obtained at f = 6.28 rad.s^{-1} (▽).

The same holds below 2% w/w for solutions of PAAxC12, although the viscosities of the hydrophobically modified chains remain slightly lower than those of the PAA10db, since in this concentration regime, hydrophobic associations mainly occur intra-molecularly and tend to reduce the hydrodynamic radius of the macromolecules.[16] Nevertheless, at low ionic strength the collapse of the chain induced by the hydrophobic aggregation is generally not very pronounced due to the strong electrostatic repulsions which dominate the conformational behaviour. On the contrary, above 3% w/w for the PAA5C12 and 4% w/w for the PAA3C12, the viscosity of hydrophobically modified polymers increases sharply due to the increasing influence of inter-chain associations.

Preparation of Hydrogels

Thiols, which can easily produce free radicals through a redox mechanism with potassium peroxodisulfate, are very good candidates to react with double bonds.[17–19] In the present case, we use a difunctional thiol, dithioerythritol ($C_4H_{10}O_2S_2$), in order to crosslink the double bonds of the PAA precursors. Modified PAA, dithioerythritol and KPS were separately dissolved in water at the desired concentration (between 3 to 8% w/w for the polymer concentration in the gel, and an equimolar quantity of thiol functions and KPS compared to the double bonds grafted on the PAA), and then are added successively to form the gel. The reaction was carried out in water, at room temperature and under atmospheric conditions.

The gels were then studied at the polymer concentration they were prepared. In these conditions where electrostatic repulsions dominate hydrophobic interactions[20] ($Q_{\text{preparation state}} \sim 16$ for 6% w/w hydrogels hydrophobically modified or not), gels are quite far from the equilibrium swelling ($Q_e \sim 85$ for the same gels).

Kinetics of Gelation

Rheological properties of the hydrogels in oscillatory shear were carried out with a stress-controlled rheometer TA Instruments AR 1000 using a cone-plate geometry with a radius of 4 cm, a truncature of 55.9 μm and a small angle of 2°.

The experiments presented were carried out at room temperature, $f = 6.28$ rad.s^{-1}, $\gamma = 1\%$.

As shown in Figure 2, 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 Figure 2) and can be correlated to the chemical gelation process which is not modified by the presence of hydrophobic groups. This important point was verified by micro-DSC measurements. Concerning the first transition (t_1), we conclude that this behaviour is mainly due to an increased viscosity of the solution caused by the hydrophobic groups.

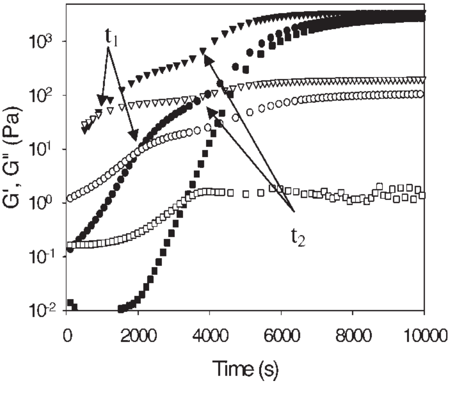

Figure 2.
Comparison of gelation for PAA10db (■ for G′, □ for G″), PAA3C12 (● and ○) and PAA5C12 (▼ and ▽) at 6% w/w. frequency: $f = 6.28$ rad.s^{-1}, deformation: 1%.

The final moduli of our hydrogels were measured once the plateau value was reached, after completion of the reaction (see Figure 2). 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 (about two decades) with increasing hydrophobic groups concentration suggesting the formation of non permanent associations introducing a dissipative mechanism independent of the solvent viscosity.

The frequency dependence of the plateau moduli was also studied for both unmodified and modified hydrogels (when the reaction is completed, a frequency sweep from 0.628 to 100 rad.s^{-1} was carried out for each gel and for various concentrations) Although all gels were predominantly elastic, unmodified PAA behaves in a nearly perfect elastic way in the range of frequencies investigated (as shown in Figure 5 for 6% w/w hydrogels, less than 2% variations on G', no significant variations on G'' as it stays extremely low compared to the G') whereas hydrophobically modified PAA displays a real frequency dependence (nearly 20% on the G' value in two decades of frequencies, almost 100% on the G'' value).

Chemical Structure of Hydrophobically Modified Hydrogels

The local structure of hydrophobic clusters was investigated by small angle neutron scattering.

SANS experiments were performed at Laboratoire Léon Brillouin, Saclay

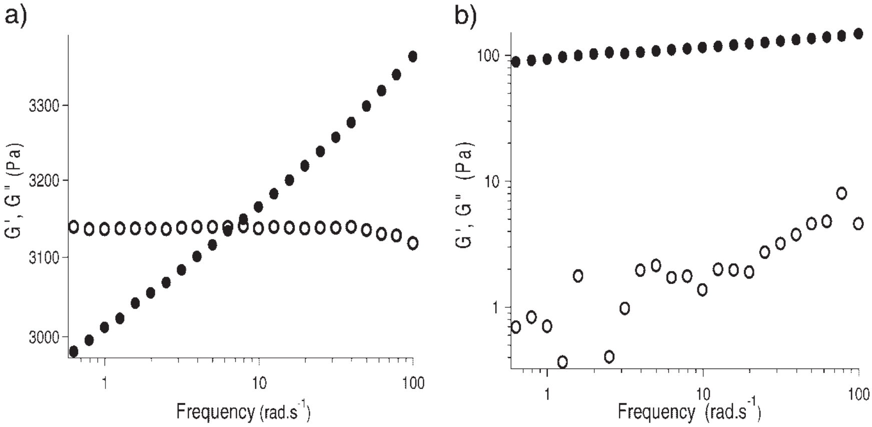

Figure 3.
Comparison of G' (a) and G'' (b) for PAA (white symbols) and PAA3C12 (black) gels at $C = 6\%$ during a frequency sweep.

(France). The experiment was carried out at $T = 20\,^{\circ}C$, using an incident neutron beam of wavelength $\lambda = 12$ Å with a corresponding sample-to-detector distance of 1.7 m. Samples were initially prepared by dissolving polymers in D_2O as solvent with or without crosslinker (dithioerythritol and KPS). The solutions were then quickly transferred into 5mm thick quartz containers for SANS experiments.

The scattering spectra reported in Figure 4 clearly demonstrate the existence of an organized structure in aqueous medium, especially for the gels: all the curves are characterized by a correlation peak which arises from the formation of interacting hydrophobic micelles. A more detailed analysis of these scattering patterns was carried out using a simple micellar model[21]: the model gives an average dry core radius $R_m \sim 18$Å of low polydispersity and an average distance between clusters of 120 Å (see fitting curves on Figure 4). The aggregation number N_{ag}, ie the number of grafts is roughly 70.

The structure of the hydrophobically modified hydrogel can be schematically seen as in Figure 5.

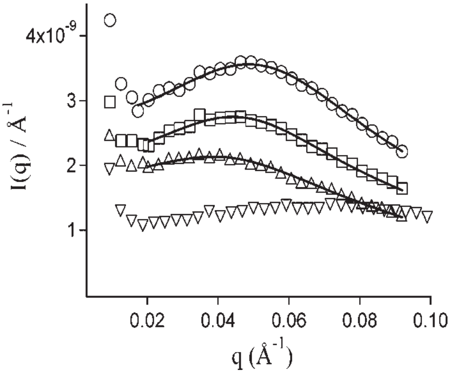

Figure 4.
Scattering profiles of PAA5C12 hydrogels and solutions in D_2O at various concentration (6%: ○, 5%: □, 4%: △, 6% solution: ▽, fits: black lines).

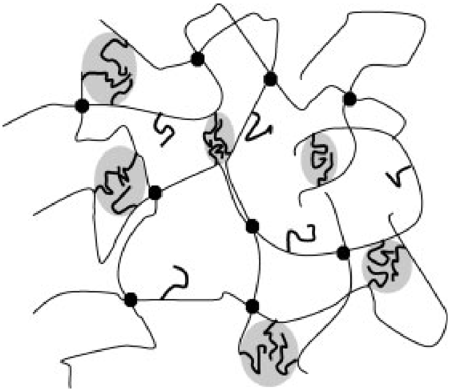

Figure 5.
Schematic structure of the hydrophobically modified hydrogel.

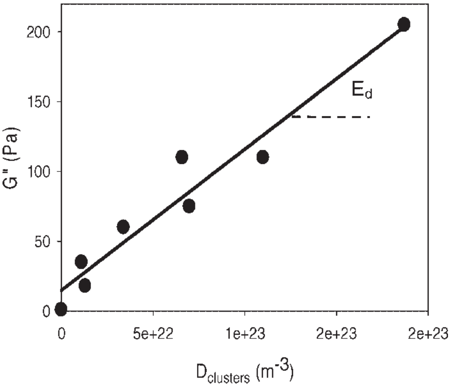

Figure 6.
Evolution of the loss modulus with the density of clusters at f = 6.28 rad.s^{-1}.

PAA chains are chemically crosslinked (small filled circles) and these crosslinks can be assumed to be small as the size of the dithioerythritol is about 5 Å. Thiol titration experiments developped[22] to investigate the effective crosslinking showed that the thiol-ene reaction was far from total (40% of thiols remain free in the gel as dangling ends). By comparing the experimental modulus obtained rheologically to the small strain shear modulus of an unentangled network in the linear regime as proposed by Obukhov et al.,[23] it appears that only about 5% of the double bonds give rise to an interchain crosslink (whereas 40% create an intraomolecular crosslink). In consequence, the distance between two crosslinks can be roughly estimated to 200 Å. Hydrophobic micelles (grey) are dispersed along the network, whereas some C_{12} chains (bold) remain in a non aggregated state.

Coming back to Figure 2, the role played by the associating clusters of hydrophobic side groups to create dissipative processes is one the most interesting results of this study. Since the size of the clusters does not appear to change much with concentration of hydrophobic groups, the main parameter should be the density of clusters per unit volume (which can be estimated from the SANS measurements) and we represented on Figure 6, the loss modulus G″ for a series of gels with increasing density of clusters at a fixed frequency (f = 6.28 rad.s^{-1}).

The loss modulus appears to increase linearly with the density of clusters as if no interactions were present between clusters. From the Figure 6, we can obtain a typical dissipative energy per aggregate, $E_d \sim 10^{-21}$ J ~ ¼ k_bT (where k_b is the Boltzmann constant and T the room temperature), which is non negligible as for example, in a rubber, the energy of an elastic segment is roughly k_bT ($G = N\ k_bT$ where N is the number of chains per unit volume).

Conclusion

We synthesized and characterised new hydrophobically modified hydrogels,[22] displaying very interesting properties as they clearly present decoupled moduli: the elastic modulus is mainly controlled by the chemical crosslinks, whereas the loss modulus is only controlled by the density of hydrophobic clusters. We expect these gels to display significantly different properties in large strain and fracture and are now working on such experiments.

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