SUPPLEMENTARY DATA

Effect of pH. The effect of the pH on the thermally-responsive properties is critical. If the pH increases above the pKa of the poly(acrylic acid) (pKa=4.2), the carboxyl group of the polymer become deprotonated, leading to a strong charge repulsion force limiting the hydrogen bonding capabilities of the microgel. Thus, it will destroy its thermally-responsive behaviour. Therefore, the effect of pH on the swelling properties of the IpnMG, rMG/2MBA and rMG/10MBA copolymer microgels samples need to be investigated. The influence of pH on swelling properties was studied by DLS. For that, microgel dispersions were prepared at constant ionic strength (0.01M) in a range of pH from 1 to 8 and measured at 20ºC. In the Figure 1, the relative swelling volume against the pH for the three samples is plotted. It can be deduced that there is not an appreciable effect of pH in the swelling behavior they almost keep a constant volume in the range of 3,5-8 pH. This result could be due to the low amount of AA in the system, 2wt% AA, this probably become deprotonated above pka, however, this is not enough to provoke the swelling of the microgel. As reported by Vincent and Bouillot who determined a decrease in the swelling behavior with the decrease of acrylic acid in poly(acrylamide-acrylic acid) microgels.

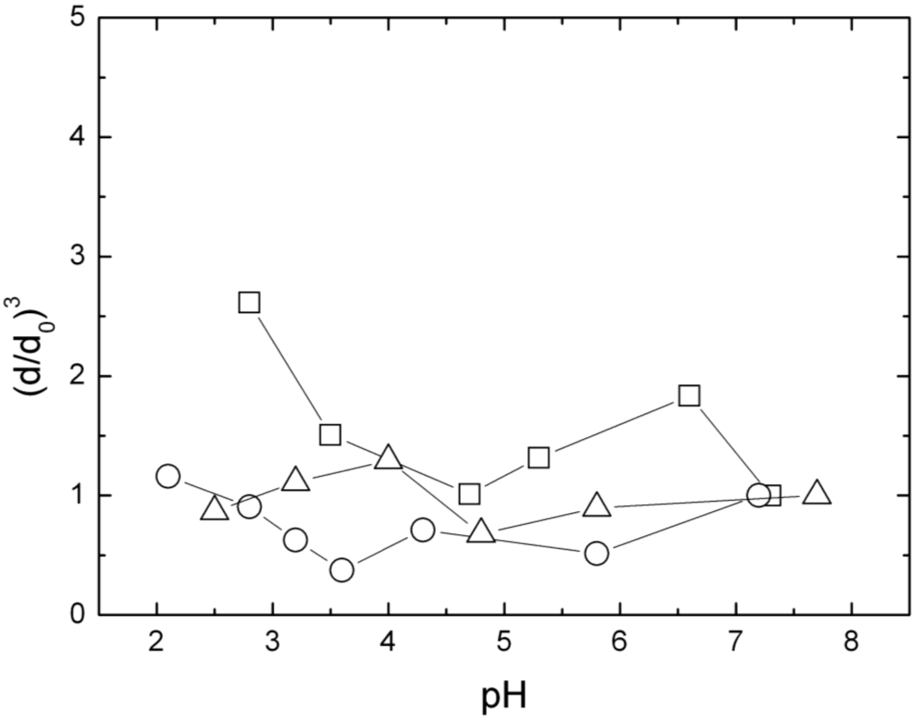

Figure 1: Evolution of the relative swelling volume $(d/d_0)^3$ with the pH measured by Dynamic Light Scattering for microgels samples, IpnMG (square), rMG/2MBA (circle) and rMG/10MBA (triangle).

Surface charge and colloidal stability.

In order to determine the effect of PEGylation in the microgels dispersions, electrophoretic mobility measurements as a function of pH were carried out. As it can be observed in figure 2, the reference microgel sample, which has not been PEGylated, keeps a decreasing trend with the increase of pH, therefore is colloidaly unstable in the studied pH range. On the contrary, an even if there is not a noticeable difference regarding the particle surface charge , PEGylated microgels at pH above pH=5 present a constant electrophoretic mobility that indicates a colloidaly stable dispersion. Therefore the PEGylation of the microgels derived in more stable systems.

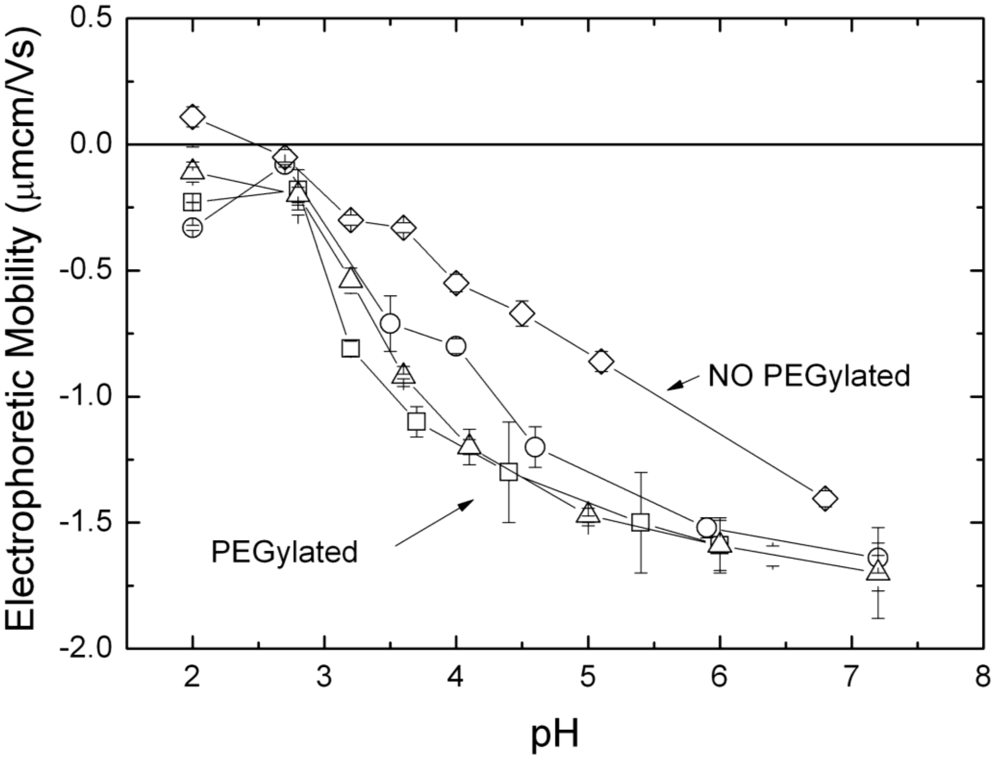

Figure 2: Evolution of the electrophoretic mobility with pH measured by Dynamic Light Scattering for microgels samples, IpnMG (square), rMG/2MBA (circle), rMG/10MBA (triangle) and no PEGylated reference sample (2%AA and 2%MBA).

Swelling behavior with temperature. The evolution of hydrodynamic diameter with temperature is shown in figure 3. The three samples, ipnMG, rMG/2MBA and rMG/10MBA, presents an increase of diameter with temperature, and hence a UCST-like transition. It is worth mentioning that at temperatures above UCST the diameter values obtained are less accurate probably due to the protocol used, and also due to the swollen state of the microgels itself. Even with this fact, the trend presented in each samples is not affected, nor the transition temperature. However the equilibrium swelling is difficult to determine and therefore, in this case, it is not possible to extract any conclusion regarding the effect of crosslinker content in the swelling behavior.

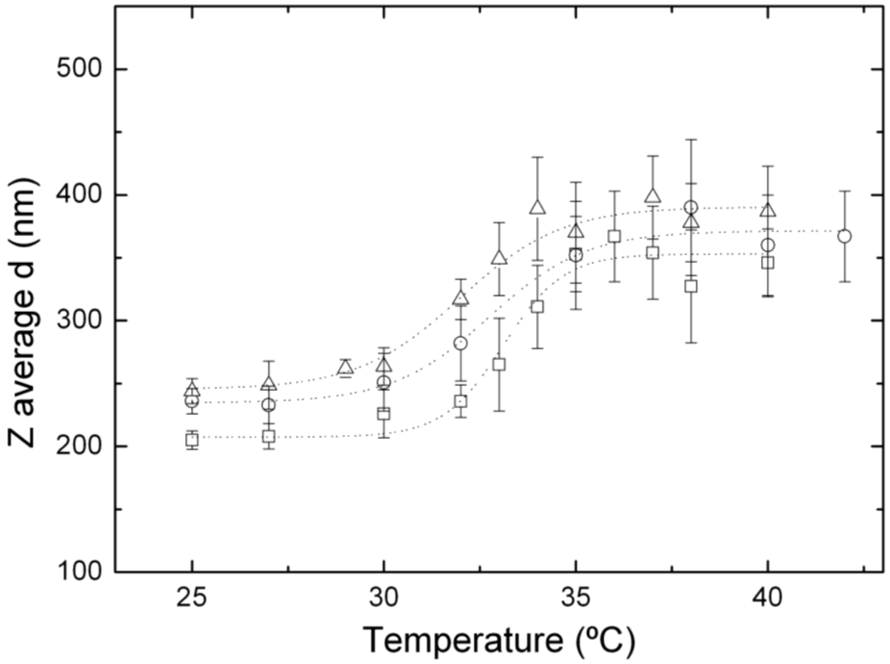

Figure 3: Evolution of the hydrodynamic Z average diameter with the temperature measured by Dynamic Light Scattering for microgels samples, IpnMG (square), rMG/2MBA (circle) and rMG/10MBA (triangle).

Determination of the number average molecular weight of the uncrosslinked polymer.

In order to determine the Mn of the microgel GPC measurement of the uncrosslinked poly(acrylamide-acrylic acid) -2%AA- 10% MBA was carried out. Figure 4 show the GPC graph in which is observed a peak at the time of 15 min that corresponds to a value of Mn =179000Da.

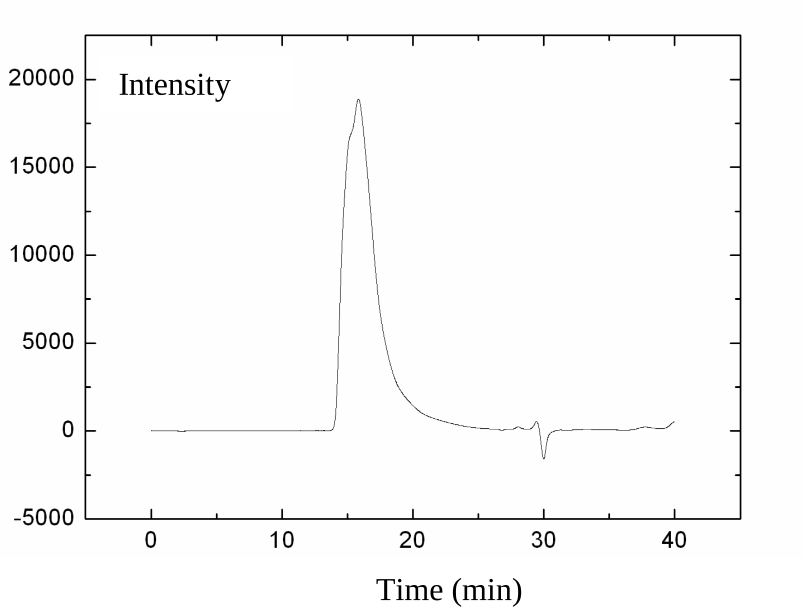

Figure 4: GPC plot corresponding to the linear polymer sample: poly(acrylamide-acrylic acid) 2%AA-10%MBA

Scaling and fractal analysis: Shih et al. and Wu and Morbidelly's theory. From the viscoelastic study, we have determined that colloidal dispersions of microgel particles behave as a solid or colloidal gel. As is known[32-33] and we have previously reported[6], in a colloidal system, small particles can come together and form large complex structures as aggregates clusters or flocs giving rise to new properties to the system such as scattering, conductivity and in our case, elasticity. The structures of colloidal gels are highly disordered but in certain length scales they are often self-similar and can be described as fractal geometries. In general, to determine the structure of a gel from rheological measurements a theoretical model is needed. For that purpose, the scaling theory that relates the structure of the gel to the rheological properties is applied. The first theory in which aggregated structures are related with their rheological properties was developed by Brown and Ball[32]. Shih et al.[33] extended this model and develop a scaling model by defining two separate regimes, strong-link and weak-link regimes:

In the *strong-link regime*, the links between aggregates (flocs) are stronger than the intrinsic elasticity of aggregates. Hence, the elastic modulus plateau (G'_0) and the limit of linearity (γ_0) or critical deformation (the deformation at which the elastic modulus starts to decrease) are related to the concentration as follows,

$$G'_0 \approx \varphi^{(d+x)/(d-D)} \tag{1}$$

$$\gamma_0 \approx \varphi^{-(1+x)/(d-D)} \tag{2}$$

where φ is the concentration , *d* is the Euclidean dimension of the system (d=3), *D* is the fractal dimension and *x* is some number that is less than the fractal dimension and larger than the unity.

For the *weak-link regime*, the elastic modulus is dominated by the elasticity of the aggregates, rather than the inter-links between aggregates. In this case, the elastic modulus and the limit of linearity are related to the concentration as follows,

$$G'_0 \approx \varphi^{(d-2)/(d-D)} \tag{3}$$

$$\gamma_0 \approx \varphi^{1/(d-D)} \tag{4}$$

This theory is able to describe this two radical situations, but the transition between these two extreme regimes could lead to intermediate situation where both inter and intra floc interaction contribute in the same way to the colloidal gel final elasticity.

In order to separate the relative importance of these two contributing factors, Wu and Morbidelli extended the model of Shih et al. by introducing microscopic elastic constant , α, to account for the relative contributions of both inter- and intra-floc links. Therefore, as a resulting of this modification, the equations relating the concentration with both the elastic modulus and the critical deformation are as follows,

$$G'_0 \approx \varphi^{\beta/(d-D)} \tag{5}$$

$$\gamma_0 \approx \varphi^{(d-\beta-)1/(d-D)} \tag{6}$$

$$\beta = (d-2) + (2+x)(1-\alpha) \tag{7}$$

where β ,is an auxiliary parameter, x is the fractal dimension of the aggregate backbone ,usually within the range of 1 to 1.3, and α is the microscopic elastic parameter comprises in the range 0 to 1. For the strong-link regime α=0 whereas for the weak-link regime α=1.