Supplementary data

Dodecyl methacrylate as a crosslinker in the preparation of tough polyacrylamide hydrogels

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Experimental procedure for the preparation of hydrogels

The hydrogels were prepared by free-radical micellar copolymerization of AAm and the hydrophobic comonomer C12 in aqueous SDS solutions at 25°C. APS (3.5 mM) and TEMED (0.25 mL / 100 mL reaction solution) were used as the redox initiator system. To illustrate the synthetic procedure, we give details for the preparation of PAAm hydrogels with 3 mol % C12 in the comonomer feed:

C12 (0.050 g) was added to the solution of SDS (0.7 g) in 8.0 mL of water and stirred for 60 min to obtain a transparent solution. After addition of AAm (0.450 g) and stock solution of TEMED (1 mL), the solution was purged with nitrogen gas for one minute. Note than longer purge times resulted extensive bubble formation in the solution. Then, stock solution of APS (1 mL) was added to initiate the reactions. For the rheological experiments, portion of this solution was transferred between the parallel plates of the rheometer. For the swelling measurements, the solution was transferred into several plastic syringes of 4 and 10 mm internal diameters and the polymerization was conducted for one day at 25°C.

Calculations of the number of hydrophobes per hydrophobic block and the number of blocks per network chain

The number of hydrophobes per hydrophobic block (N_H) and the number of blocks per network chain (S) were estimated from the concentration ratio of C12 (HM) to the surfactant (SDS) by [1]:

$$N_H = \frac{[HM]\bar{N}_{Agg}}{[SDS]-CMC} \qquad (1a)$$

$$S = \frac{f_{HM}\, N}{N_H} \tag{1b}$$

where N_{Agg} is the aggregation number of the surfactant SDS (62, [2]), CMC is its critical micelle concentration, f_{HM} is the mole fraction of C12 in the comonomer feed and N is the elastically effective network chain length of the associating hydrogels. Solution of Eq. (1b) requires the effective chain length N of the network chains. Assuming that the elastic modulus G' at high frequencies equals to the equilibrium shear modulus G, one may estimate the effective length N of the network chains. For a phantom tetrafunctional network, G at the state of gel preparation is given by

$$G = 0.5\left(\frac{\rho}{\overline{M}_c}\right) R\,T\,\nu_2^0 \tag{2a}$$

$$N = \overline{M}_c / \overline{M}_r \tag{2b}$$

where ρ is the polymer density $\overline{M}_c$ is the molecular weight of the network chains, $\overline{M}_r$ is the average molecular weight of the repeat units, ν_2^0 is the volume fraction of crosslinked polymer in the gel, R and T are in their usual meanings [3,4]. Since $\rho\nu_2^0$ was set to 50 kg/m^3 in our experiments, from the elastic moduli of hydrogels at the frequency ω = 151 rad/s together with Eqs. (1b), (2a), and (2b), the number N_H of hydrophobes per block and the number S of hydrophobic blocks per network chain were estimated.

References

[1] Regalado EJ, Selb J, Candau F. Macromolecules 1999;32:8580.

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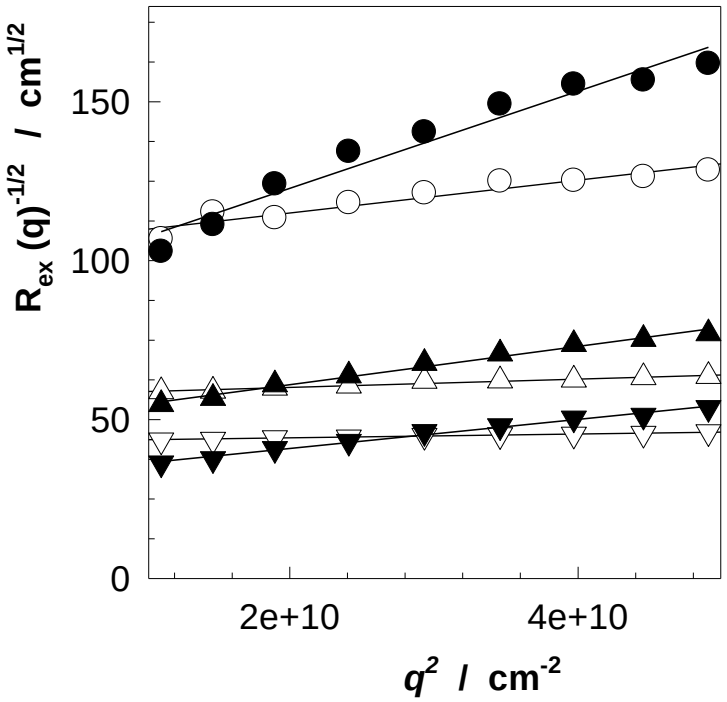

Fig. S1. DB plots for PAAm gels just after their preparation formed by C12 (filled symbols) and BAAm (open symbols). The gels are at the state just after their preparation. C12 = 3 (●), 4 (▲), and 5 mol % (▼). BAAm = 0.54 (○), 1.1 (△), and 1.5 mol % (▽).

We have to note that, in the treatment of the scattering data of gels, the total structure factor is described by the sum of dynamic and static components. The dynamic component originates from thermal concentration fluctuations equivalent to those observed in solutions, which can be described by a Lorentz function. The latter component, also known as excess scattering, originates from permanent (frozen-in) spatial fluctuations of polymer concentration fixed by crosslinks. In the present work, the excess scattering data were analyzed within the framework of the DB theory. This theory was developed for describing heterogeneous media, like inhomogeneous gels containing highly crosslinked individual domains on length scales in the range of 10 – 100 nm in a continuous less crosslinked medium. In this approach, one postulates an exponential form for the spatial correlation function of the number density of scatterers, which leads to a Lorentzian squared for the scattered intensity (Eq. (1) in the text). Previous works indeed show that the excess scattering data of gels obtained from light scattering and SANS measurements are well described by the DB expression (e.g., refs. 17, 18, 21 in the text).

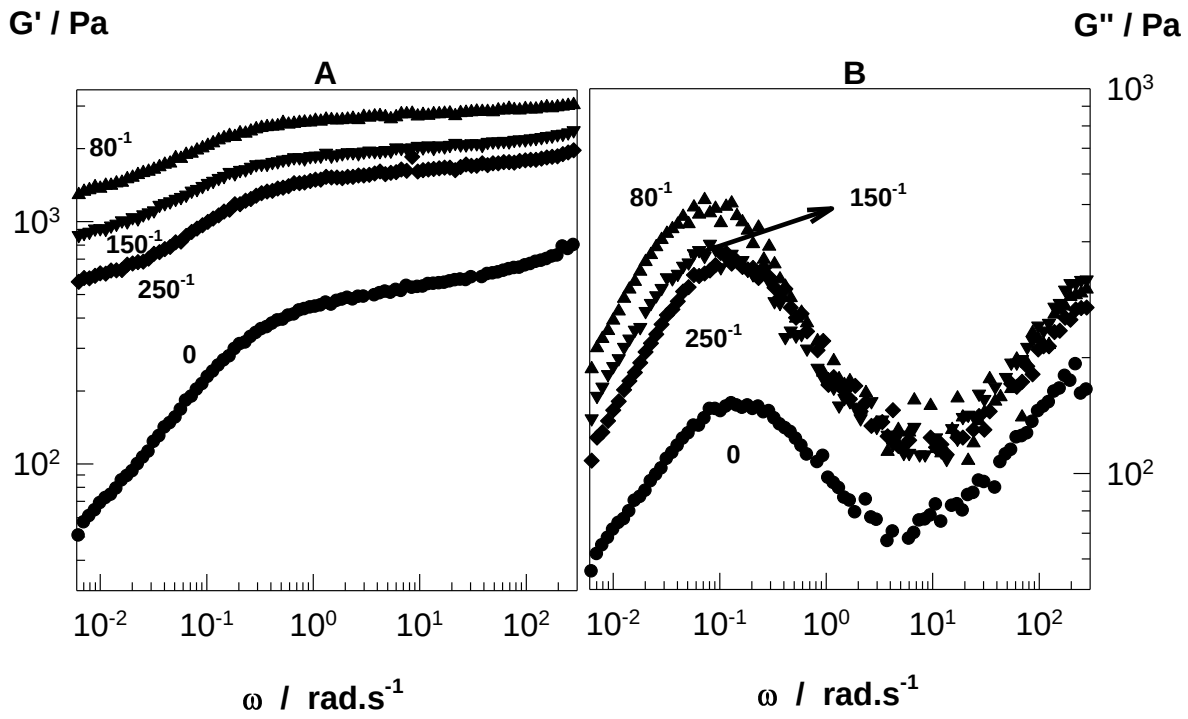

Figure S2. *G'* (A) and *G''* (B) of PAAm hydrogels containing 1 mol % C12 shown as a function of the frequency ω measured after 2h of reaction time. $\gamma_o = 0.01$. SDS = 7 %. $X = 0$ (●), 1/250 (◆), 1/150 (▼), and 1/80 (▲).