1. Figure SI1 and Figure SI2 are the resolution graphs of Figure 1(a4) and Figure 1(b4) respectively. Video 1 is the three-dimensional reconstruction video at the position of pore walls which is shown in Figure SI1. Video 2 is the three-dimensional reconstruction video of the pore walls. The staining method of the cryogel shown in video 2 is inverse comparing with the original method in the manuscript. The primary PNIPA network was stained by Rhodamine B while the secondary PAAm network was stained by FITC.
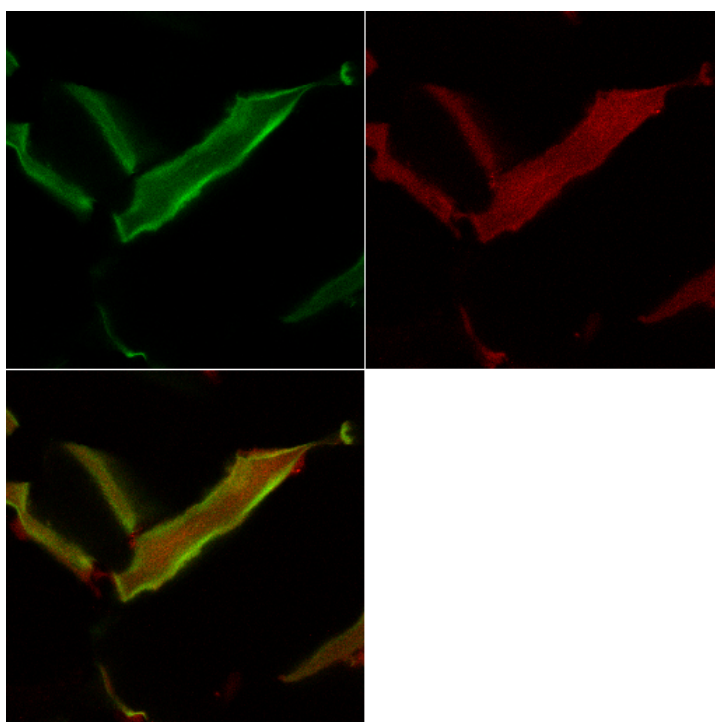

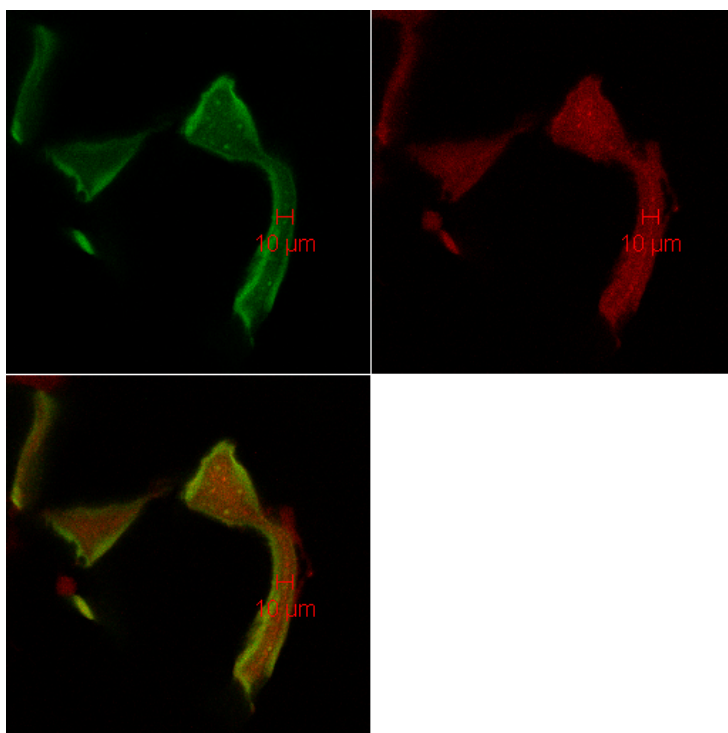Figure SI1. Resolution graphs of Figure 1(a4)

Figure SI2. Resolution graphs of Figure 1(b4)

2. When preparing DN cryogels, degradable crosslinkers are used to prepare the primary networks according to the reference (M. Andac, Macromol. Chem. Phys. 2008, 209, 577–584). The secondary networks remain undegradable. The primary networks are then completely degraded into linear polymer chains after the DN cryogels have been prepared, so that morphology of the secondary network would be studied separately. Figure SI3 shows the SEM morphology of the section of the pore walls. If there is a microphsae separation between the primary and the secondary networks, there should be gaps or a lot of pores in the section which are generated as a result of the washing out of the degraded primary network. However, No significant difference can be found between Figure SI3 and Figure 2(b4) in the manuscript. It indicates that the degraded primary network (namely linear polymer chains) is immobilized in the secondary network homogeneously. So, no microphase separation occurs between the primary and the secondary networks.
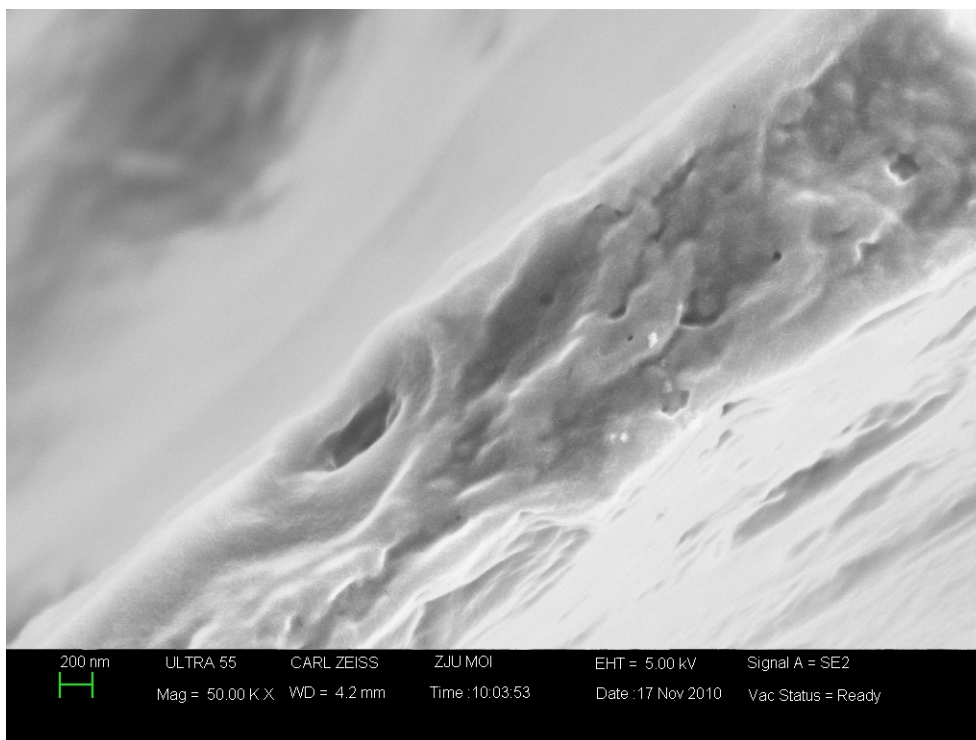
Figure SI3. SEM morphology of the section of the pore walls of degradable DN cryogel

3. Figure SI4 is the SEM image of the surface morphology of conventional nonporous hydrogels which are prepared using homogenous initiation. It can be seen that there is no holes on the surface. It indicates that the holes which are showed in Figure 2(a3) and Figure 2(b3) should be generated as a result of the washing out of the residual (unreacted or partial unreacted) heterogenous initiator DDBAPS aggregates.
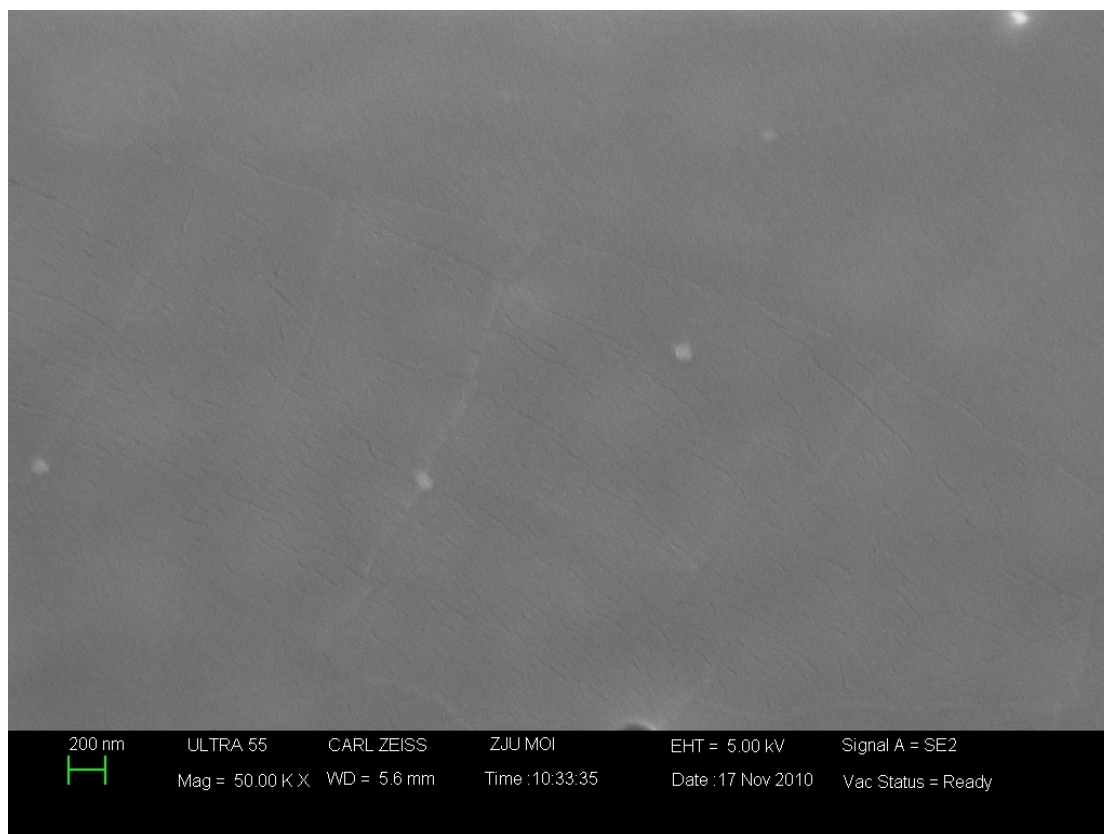
Figure SI4. SEM image of the surface morphology of conventional nonporous hydrogels

4. There are two evidences that can support the mechanistic explanation of the improved mechanical property of the ionic DN cryogels as shown in Figure 7 in the manuscript. The first evidence is shown as follows. When preparing DN cryogels, the authors are using degradable crosslinkers to prepare the primary networks. The secondary networks remain undegradable. The primary networks are then completely degraded into linear polymer chains after the DN cryogels have been prepared. The swelling ratio of the degraded ionic DN cryogel is approximatively 1.5 times as large as that of the undegraded ionic DN cryogel. It indicates that the whole network of the undegraded ionic DN cryogel is restrained by the primary network. The other evidence is shown as follows. The small amplitude shear experiments of D-DN are performed contrastively at 25 °C and 40 °C. Theoretically, the shear modulus will increase with temperature for a certain sample (Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953). But for D-DN, G' is around

25 kPa at 25 °C and 21 kPa at 40 °C. This is because the lower critical solution temperature (LCST) of PNIPA is around 32 °C and the primary PNIPA network trends to shrink at the temperatures higher than 32 °C. It is considered that the force of the shrink trend partly counteract the electrostatic repulsion between the anionic carboxyl groups.