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Nanoscale TEM Imaging of Hydrogel Network Architecture

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Supporting Information

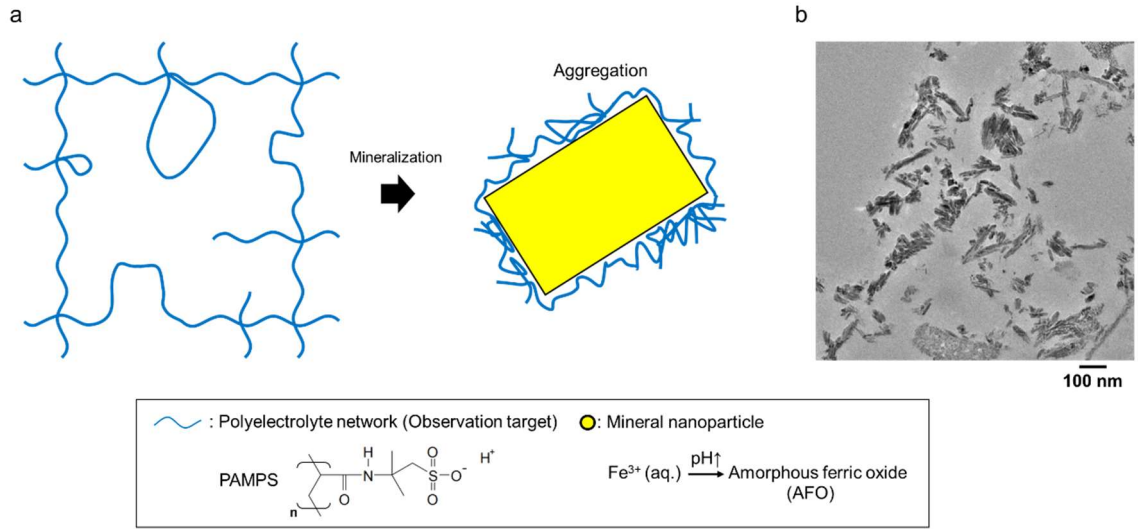


Figure S1. (**a**) Schematic illustration of the mineral staining for a polyelectrolyte network without skeleton network causing a fatal collapse and aggregation of the polymer network strands. (**b**) TEM image of the stained PAMPS-4 gel in the absence of skeleton. Lage minerals (tens ~ hundreds nm) were formed and network like structures were not observed due to aggregation by staining.

Table S1. Young's modulus of PAMPS gels in as-synthesized state (E_0), thickness swelling ratio (λ_s) of PAMPS networks in relative to their respective as-synthesized state and the average mesh size ξ of networks in water and in TEM specimen. The mesh sizes were estimated from E_0 and λ_s using Eqs. 1 and 2. Since the swelling ratios and mesh sizes in water and in TEM specimen are almost the same, the values in water are used in the text.

	As-prepared state	in water		in TEM specimen	
PAMPS-C_x	E_0 (MPa)	λ_s (−)	ξ (nm)	λ_s (−)	ξ (nm)
PAMPS-1	0.01	4.5	51	4.8	54
PAMPS-2	0.03	3.2	26	3.2	26
PAMPS-3	0.04	2.6	17	2.7	18
PAMPS-8	0.07	1.7	10	1.6	9

Table S2. Thickness swelling ratio (λ_s) of PDMAAm-0.1 network in TEM specimen in relative to its as-synthesized state in PAMPS-C_x networks, and the corresponding average mesh size ξ of PDMAAm-0.1 network in TEM specimen estimated from λ_s and E_0 using Eqs. 1 and 2. The Young's modulus of PDMAAm-0.1 network gel in as-synthesized state (E_0) was 0.02 MPa.

	in TEM specimen	
Sample	λ_s (−)	ξ (nm)
in PAMPS-1	1.2	10.0
in PAMPS-2	1.0	8.1
in PAMPS-3	1.1	8.8
in PAMPS-8	0.9	7.5

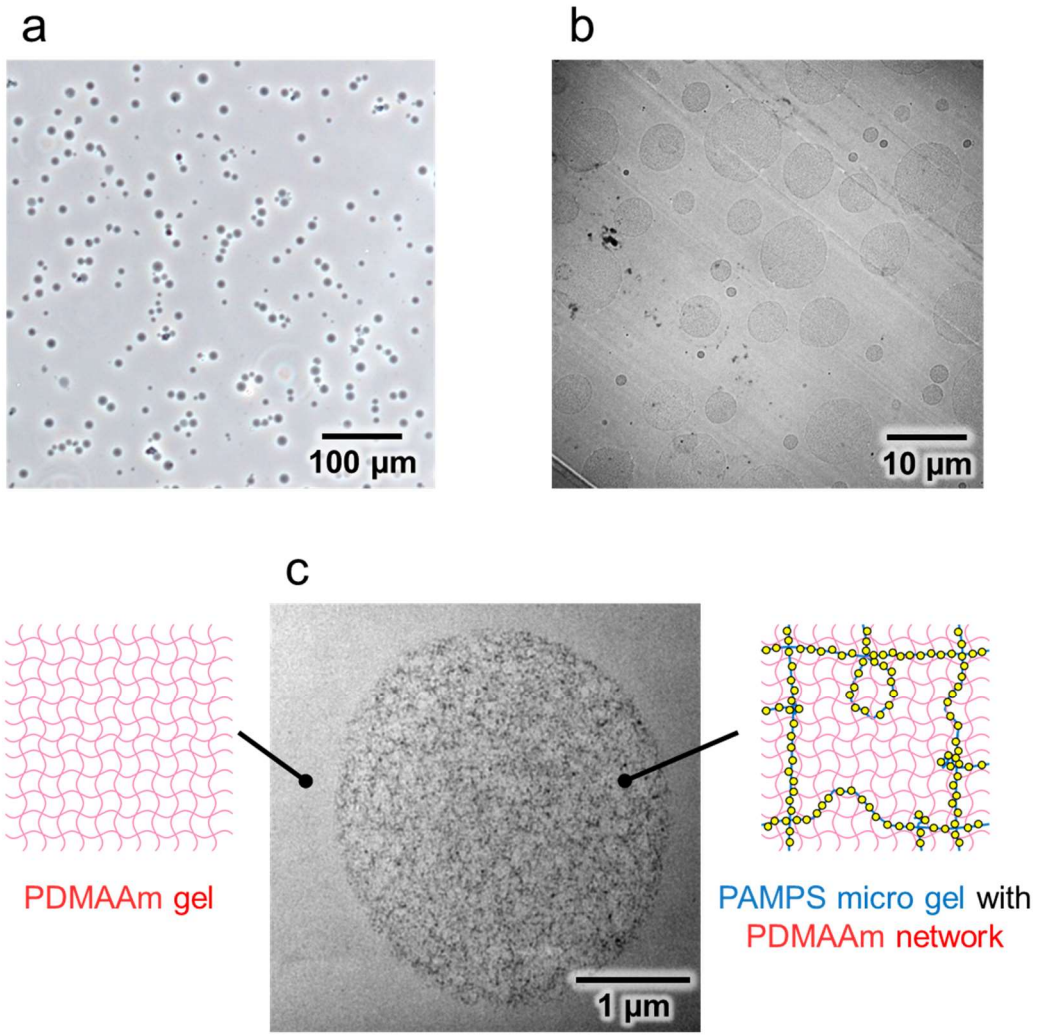


Figure S2. TEM image of the PAMPS-4 micro gels embedded in the bulk PDMAAm gel. (**a**) Optical microscopy image of the pristine PAMPS micro gel particles. (**b**) Low magnification TEM image. (**c**) High magnification TEM image with schematic illustrations. Mineral nanoparticles only are formed on the polyelectrolyte PAMPS network.

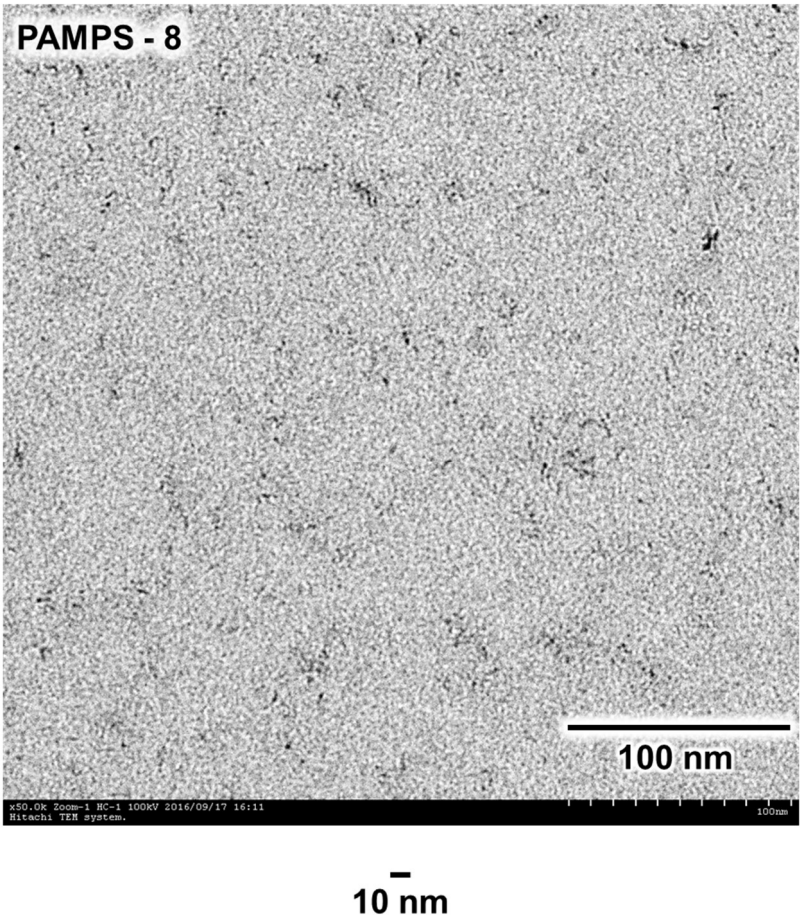


Figure S3. TEM image of the PAMPS-8 network. The mesh size calculated from PAMPS gel bulk modulus (**Table S1**) is shown by bar in the bottom. Only isolated mineral dots and strand fragments are observed, and the connected polymer mesh was not observed, indicating under-staining of network.

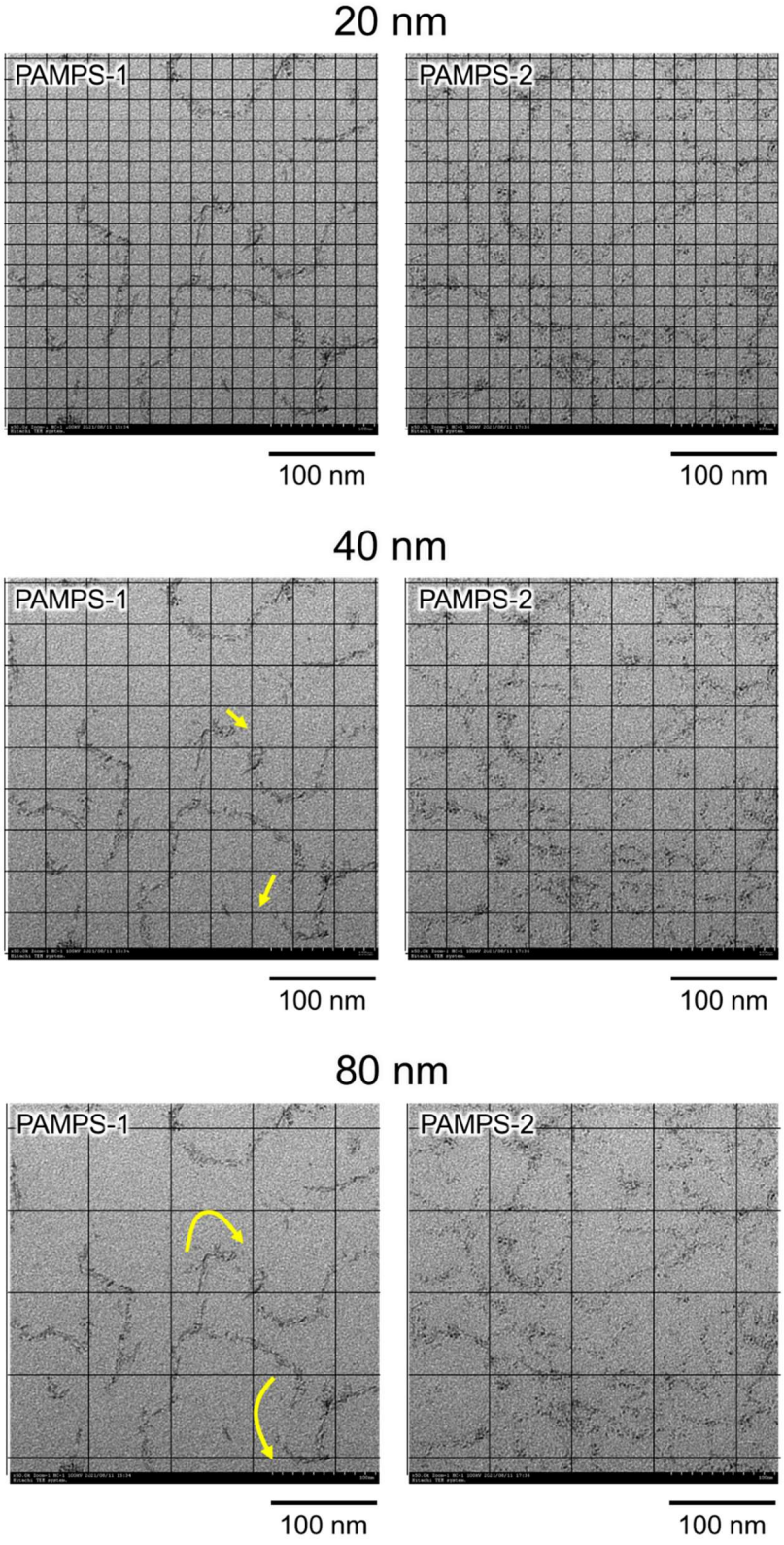


Figure S4. A facile method to determine the persistence length of a stained polymer strand

from TEM images in this work. Square lattices of different sizes were placed on the TEM images of PAMPS networks. The largest square size, in which a polymer strand does not bend, is determined as the persistent length of the stained polymer strand in the PAMPS network. The images show that in 80 nm square, polymers bend frequently, but in 40 nm square all polymers are in straight lines (see yellow arrows in the figure). Thus, the persistent length is determined as 40 nm. The numbers above the TEM images are lengths of square lattices in the respective TEM images. Samples are coded as PAMPS-C_x, where C_x stands for the crosslinker ratio (mol%).

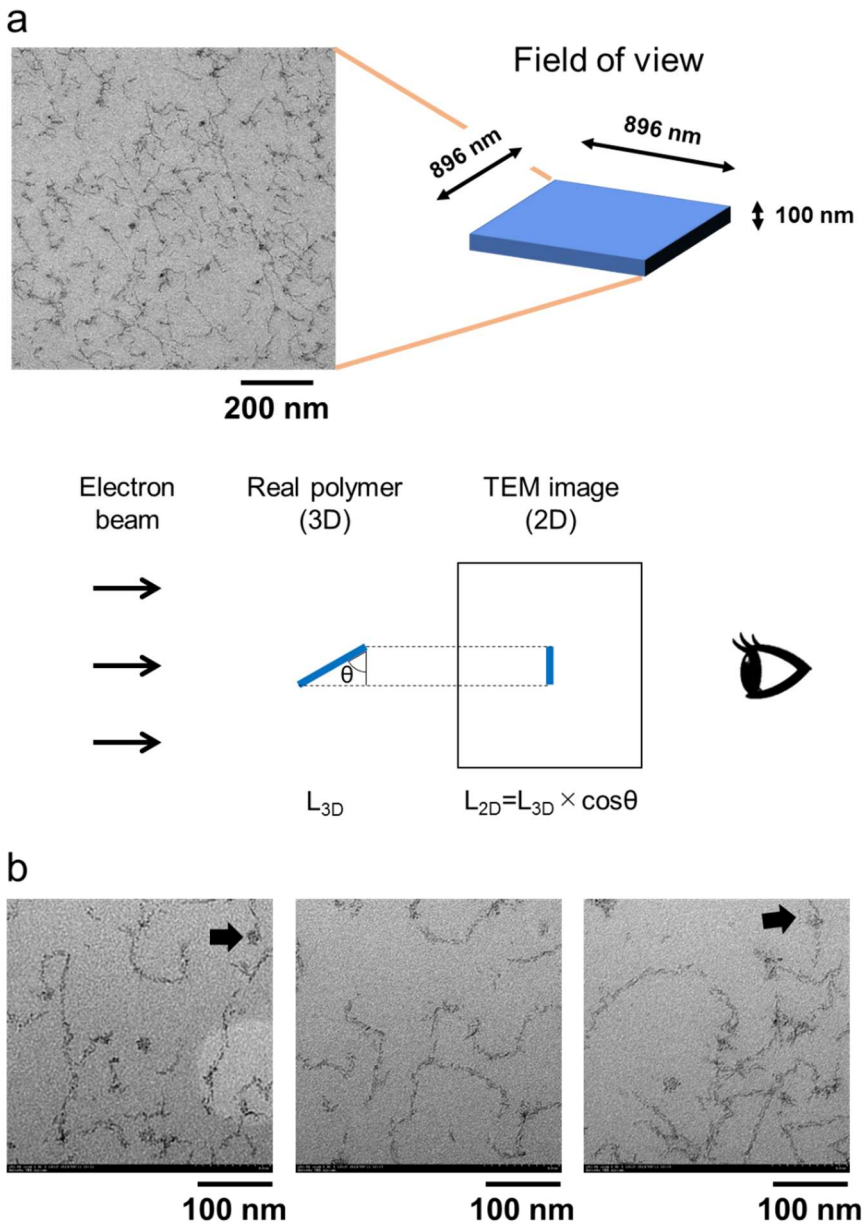


Figure S5. (**a**) Illustration to show calculation process of the polymer length in the TEM field of view for the PAMPS-1 gel. (**b**) High magnification TEM images of the PAMPS-1 network at different locations. The mesh structures sized in tens to hundreds of nanometres were clearly observed. The large aggregations indicated by black arrows are ascribed to dangling chains on the network.

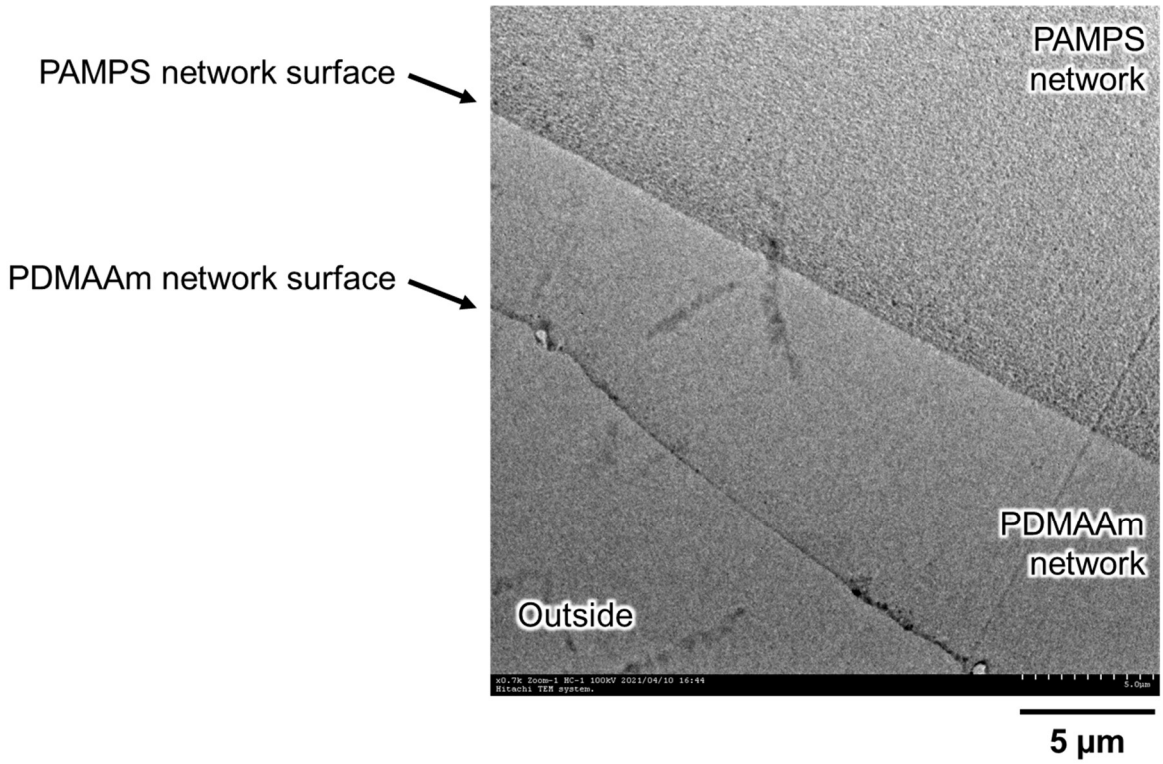
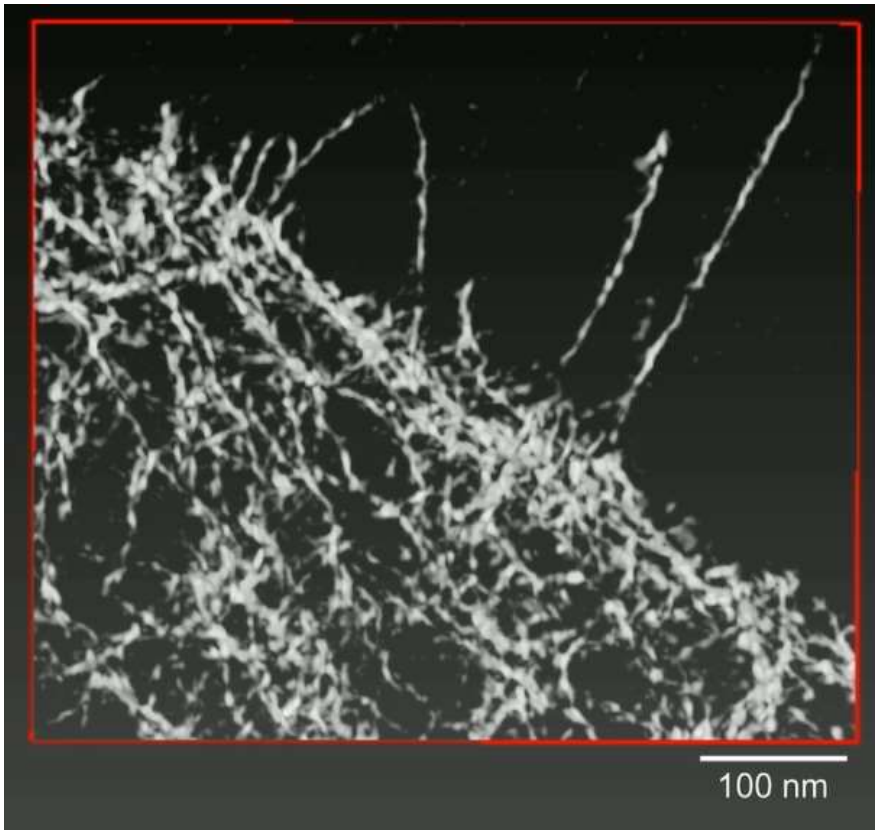


Figure S6. Low magnification TEM image to show PAMPS-3 surface. PAMPS network in swollen state is clearly stained by AFO. We can also see PDMAAm skeleton network surface because some AFO particles mineralized at outside of gel precipitated on PDMAAm network surface. The thickness of the PDMAAm network layer swollen in water varies depending on the location (usually surface PDMAAm layer thickness is 5 to 20 μm).



Supplementary Video 3D TEM movie of the PAMPS-4 network. A porous PAMPS gel was used.