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Towards the development of multifunctional hybrid fibrillary gels: production and optimization by colloidal electrospinning

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Supporting information

1. Experimental section

1.1. Materials

N-isopropylacrylamide (NIPAAm, Aldrich Chemistry, 97%) was used as a monomer and N,N-methylene bis-acrylamide (MBA, Sigma-Aldrich, 99%) as cross linker, ammonium persulfate was chosen as initiator (APS, Sigma-Aldrich, 99%) and sodium bisulfite (SBS, Acrös Organics) as catalyst. Acrylic acid 90% (Alfa Aesar) was used in order to study the effects in the microgels' LCST. PVP (Sigma-Aldrich, Mw = 1.300.000) was used as a fiber template to produce the non-woven mats.

All reagents were used as received without any further purification.

1.2. Conditions for the synthesis of PNIPAAm based microgels

Reagents	wt% monomer	Mass (g)	Volume (mL)
NIPAAm	100	1	20
MBA	5	0.05	20
APS	10	0.1	20
SBS	5	0.05	20
			80 + 20 mL H_2O

Since acrylic acid comes in liquid form and its density is 1.05 g.cm^{-3}, upon synthesis of PNIPAAm-AAc microgels the volume of AAc corresponding to 6 and 10 wt% (regarding PVP mass) is 57.1 and 95.2 µL, respectively.

1.3. Microgels characterization

Dynamic light scattering (DLS) technique was used to determine the microgels' hydrodynamic diameter and to study their behavior at different temperatures. The equipment used is a Horiba Nanopartica Analyzer SZ-100 equipped with a 594 nm He-Ne laser and a Peltier element to control the temperature. All measurements were carried out for diluted suspensions (1 mg.mL^{-1}) at a temperature range from 22 – 46ºC in disposable cuvettes.

2. Results

2.1. Hydrodynamic diameters of PNIPAAm and PNIPAAm-AAc microgels

Table 1. Hydrodynamic diameter (D_h) and polydispersity index (PI) values for synthesized microgels measured by DLS at 24 and 40ºC. All measurements were performed at pH 5.6.

Sample	24ºC		40ºC	
	D_h (nm)	PI	D_h (nm)	PI
MG[1]	223 ± 53	0.97	48 ± 6.3	0.34
MG6AAc[2]	346 ± 32	0.68	28 ± 6.4	0.43
MG10AAc[3]	387 ± 139	1.07	65 ± 12	0.32

[1] PNIPAAm microgels

[2] PNIPAAm microgels with 6 wt% of acrylic acid (with respect to NIPAAm mass)

[3] PNIPAAm microgels with 10 wt% of acrylic acid (with respect to NIPAAm mass)

2.2. PVP UV crosslinking mechanisms

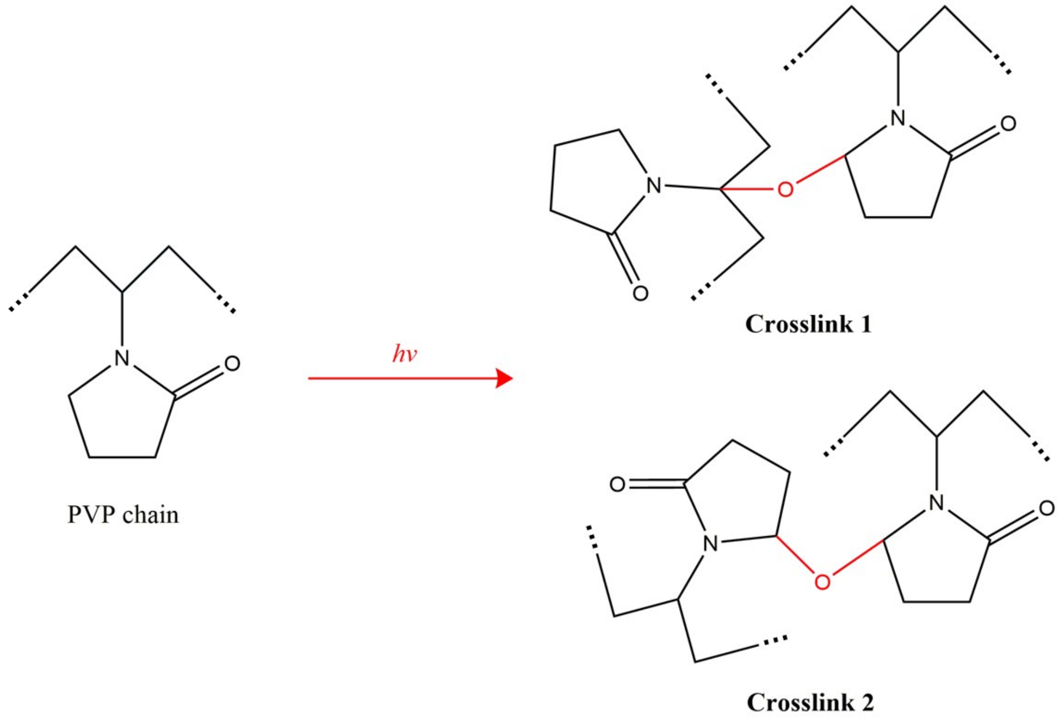

Figure 1 - Chemical structure of N-vinylpyrrolidone monomer and effect of UV irradiation on PVP chain with consequent intramolecular crosslinked PVP.

2.3. MFD of PVP and composite fibers after UV irradiation

Table 2. PVP and composite membranes MFD variation with UV irradiation time.

UV irradiation (min)	PVP MFD (nm)	Composite MFD (nm)
5	823 ± 50	554 ± 64
10	856 ± 111	511 ± 65
15	833 ± 69	579 ± 109
20	665 ± 49	543 ± 69
30	741 ± 82	532 ± 45
40	871 ± 64	509 ± 60
60	817 ± 46	497 ± 78

2.4. Molecular weight of the polymer chain between two neighboring crosslinking nodes and mesh size

Table 3. Variation of the molecular weight of the polymer between two neighboring crosslinking nodes, mesh size and crosslinking density with the UV irradiation time for PVP and composite non-woven mats. The values were calculated considering the swelling ratio at 3h for all samples.

UV irradiation (min)	PVP			Composite		
	5	**30**	**60**	**5**	**30**	**60**
$\bar{M}_c$ **(Da)**	10168	27.2	12.3	3704	11.8	33.7
ξ **(nm)**	6468	18.2	19.3	2516	8.8	49.7
ρ_x **(10^{-5} mol.cm^{-3})**	4723	14.2	26.5	1863	7.1	67.1