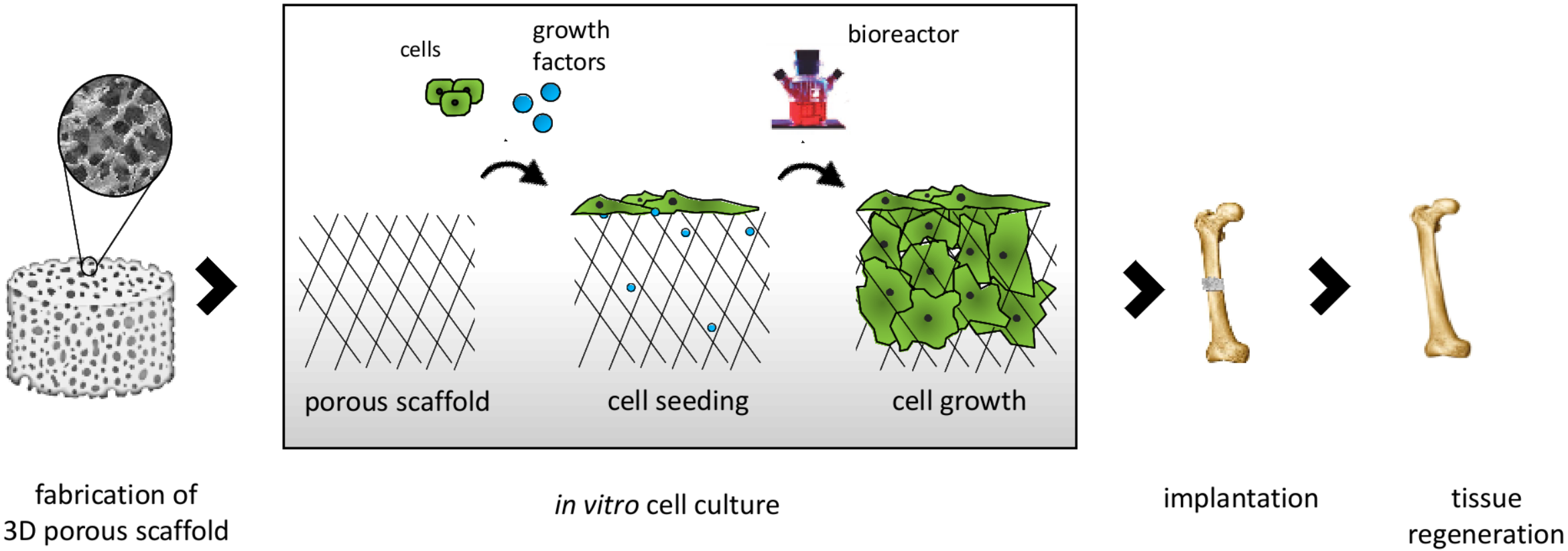
Rheology of Photo-crosslinkable Acrylate-endcapped Urethane-based Polymers

ESR12: Yanzhao Li

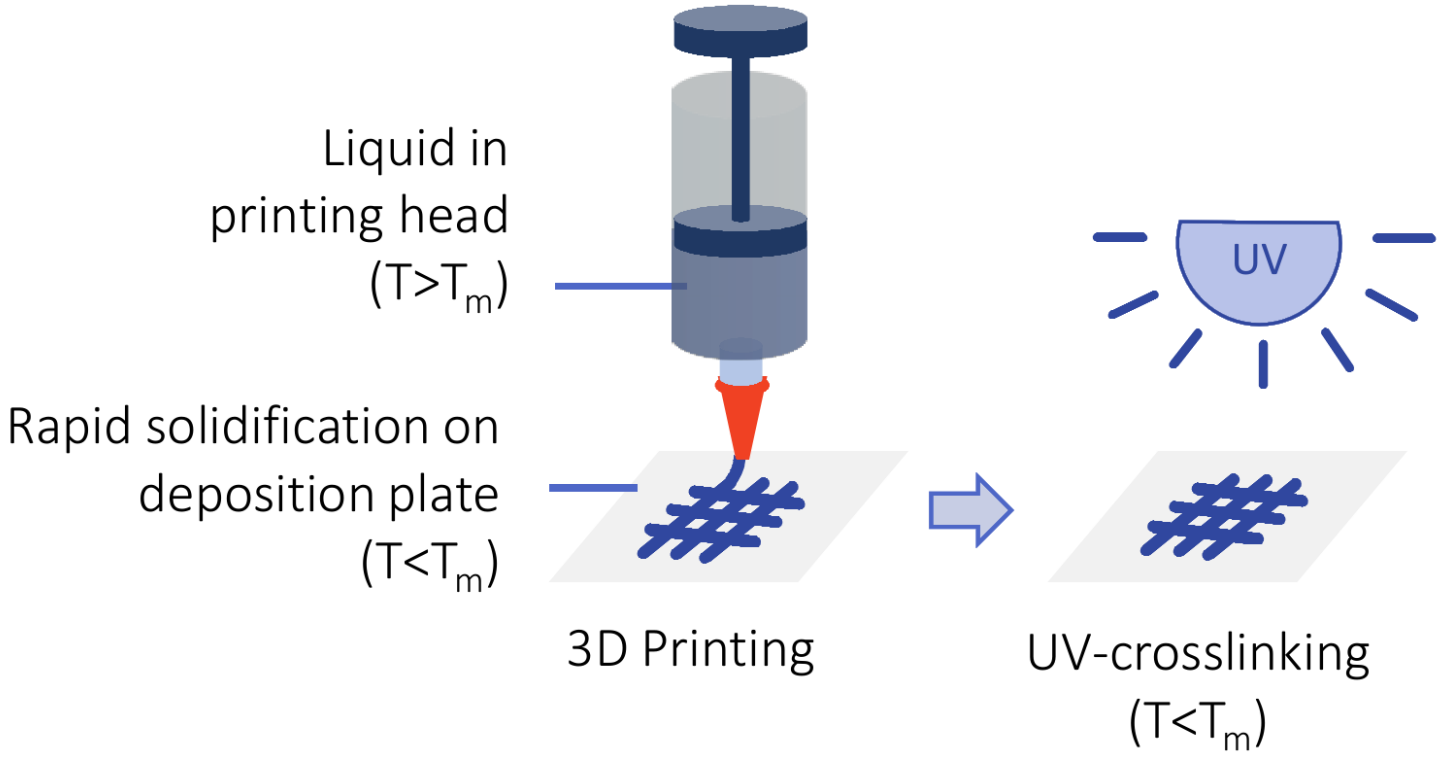
Supervised by Dr. Patrice Roose and Prof. Evelyne Van Ruymbeke

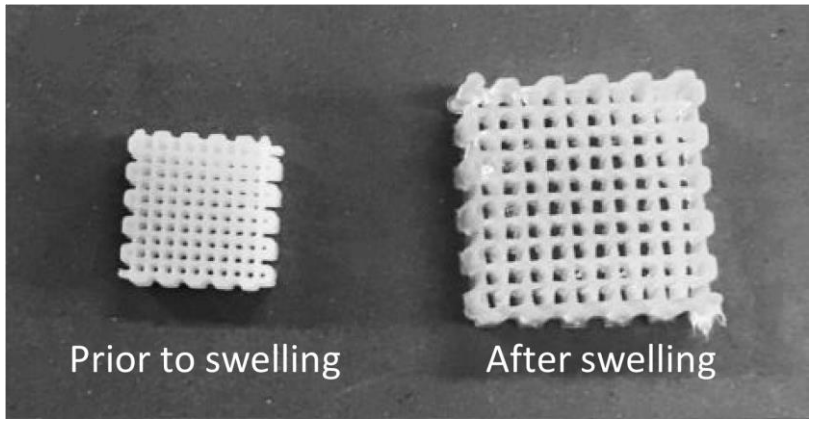
Scaffold-based Tissue Engineering



Aysu Arslan. PhD thesis, Ghent University, 2020

Extrusion-based 3D Printing





Scaffold for meniscus implantation

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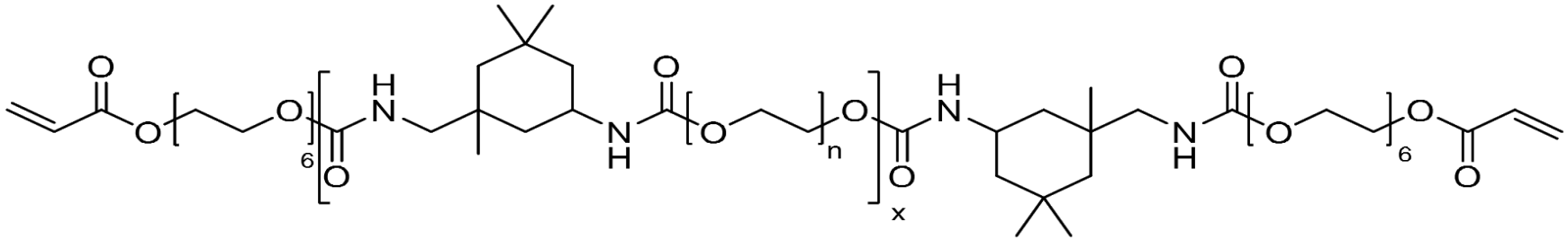
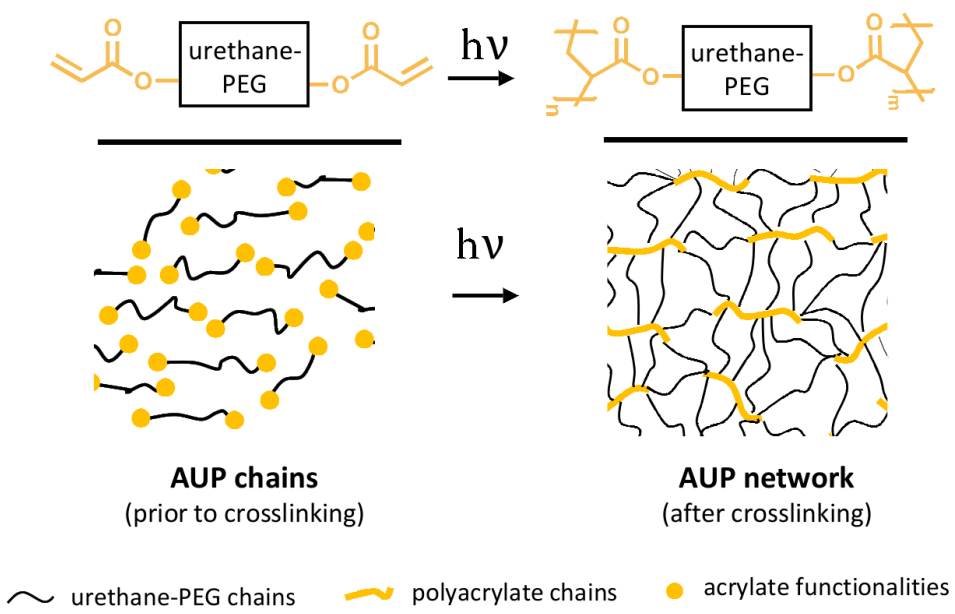
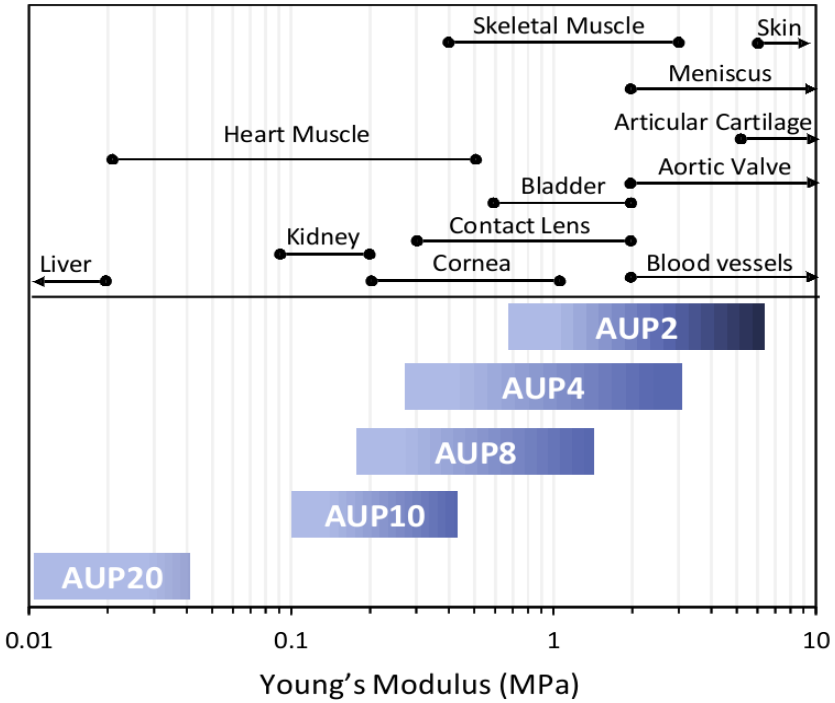
Acrylate-endcapped Urethane-based Polymers (AUP)

Crosslinkable Groups	Spacer	Urethane	Backbone	Urethane	Spacer	Crosslinkable Groups



Backbone: **AUP2k**(PEG: 2000 g/mol) **AUP10k**(PEG: 10000 g/mol) **AUP20K**(PEG: 20000 g/mol)





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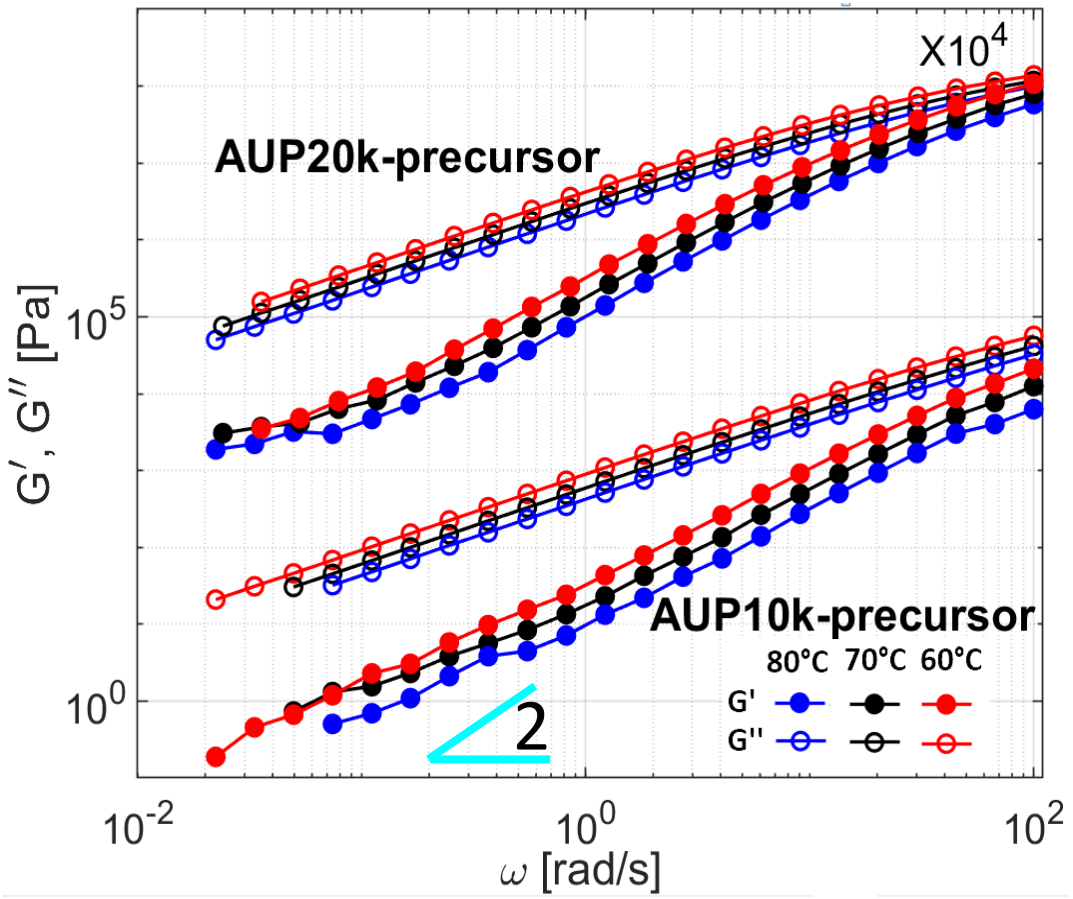
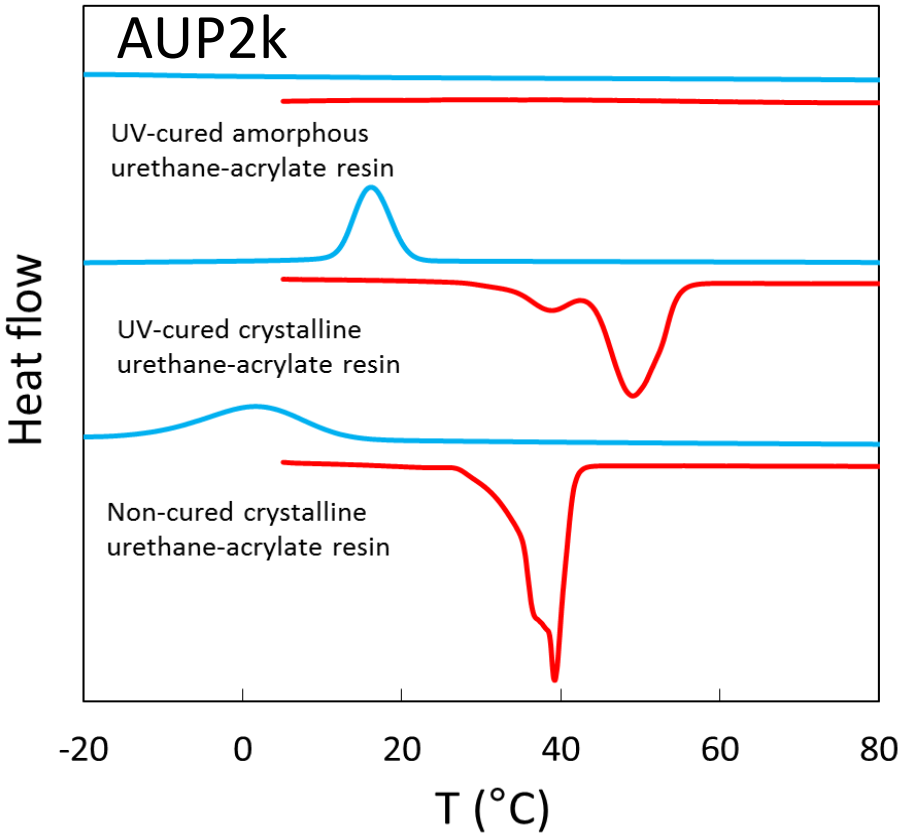
AUP Precursors



Both samples show liquid-like viscoelastic behavior. The terminal relaxation of both samples is not reached.

Objectives

Understanding the dynamics of AUP networks photo-crosslinked either in solid state(20℃) or in molten state(70℃).



(Annemie Houben, etc. Materials Today Chemistry, 2017,4, 84-89)

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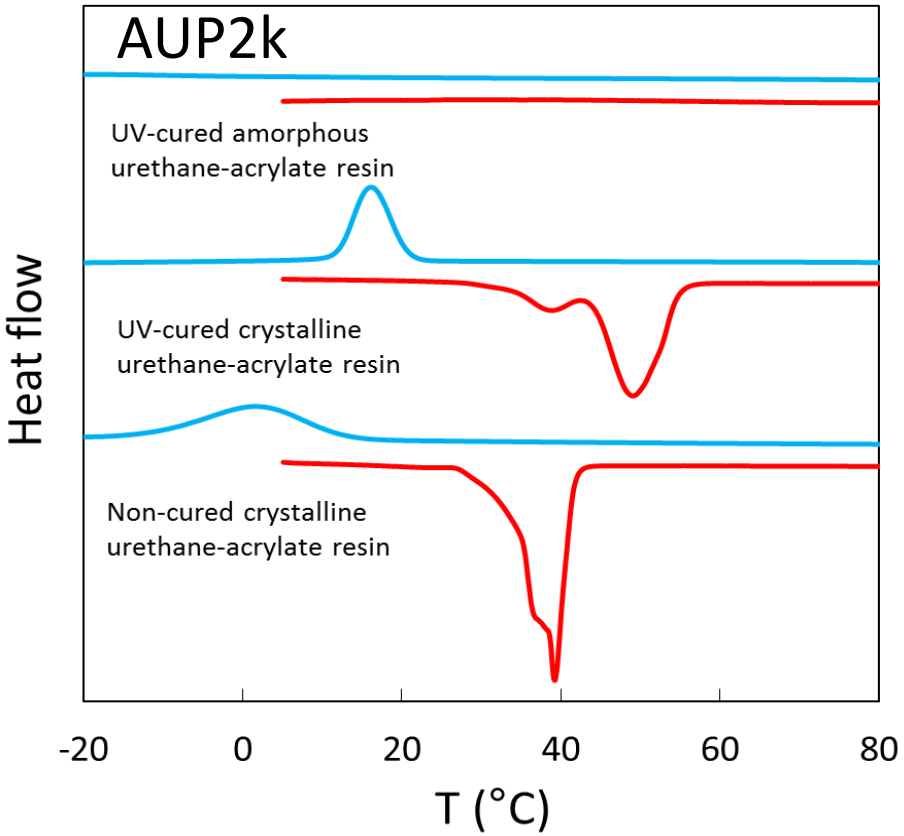

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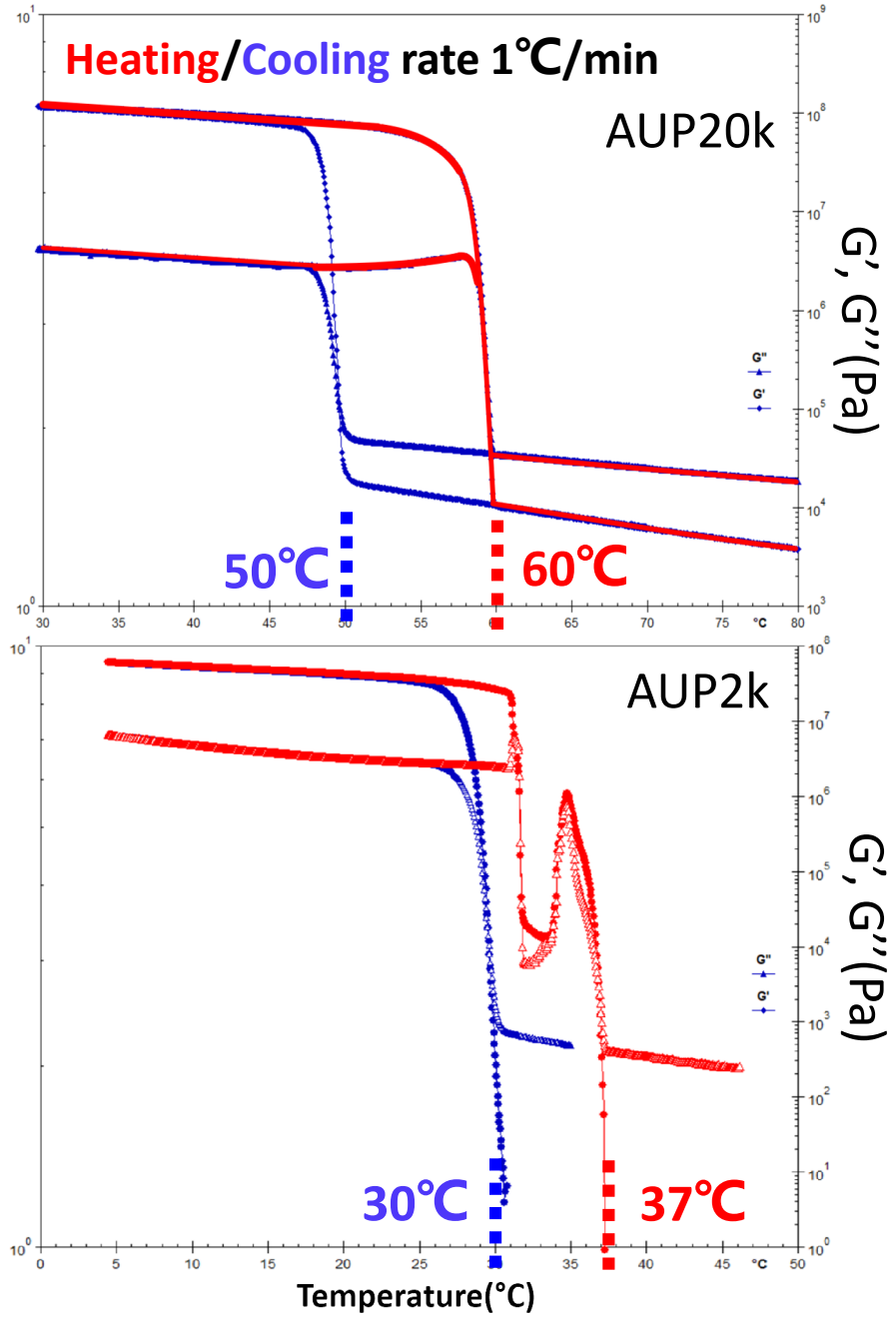
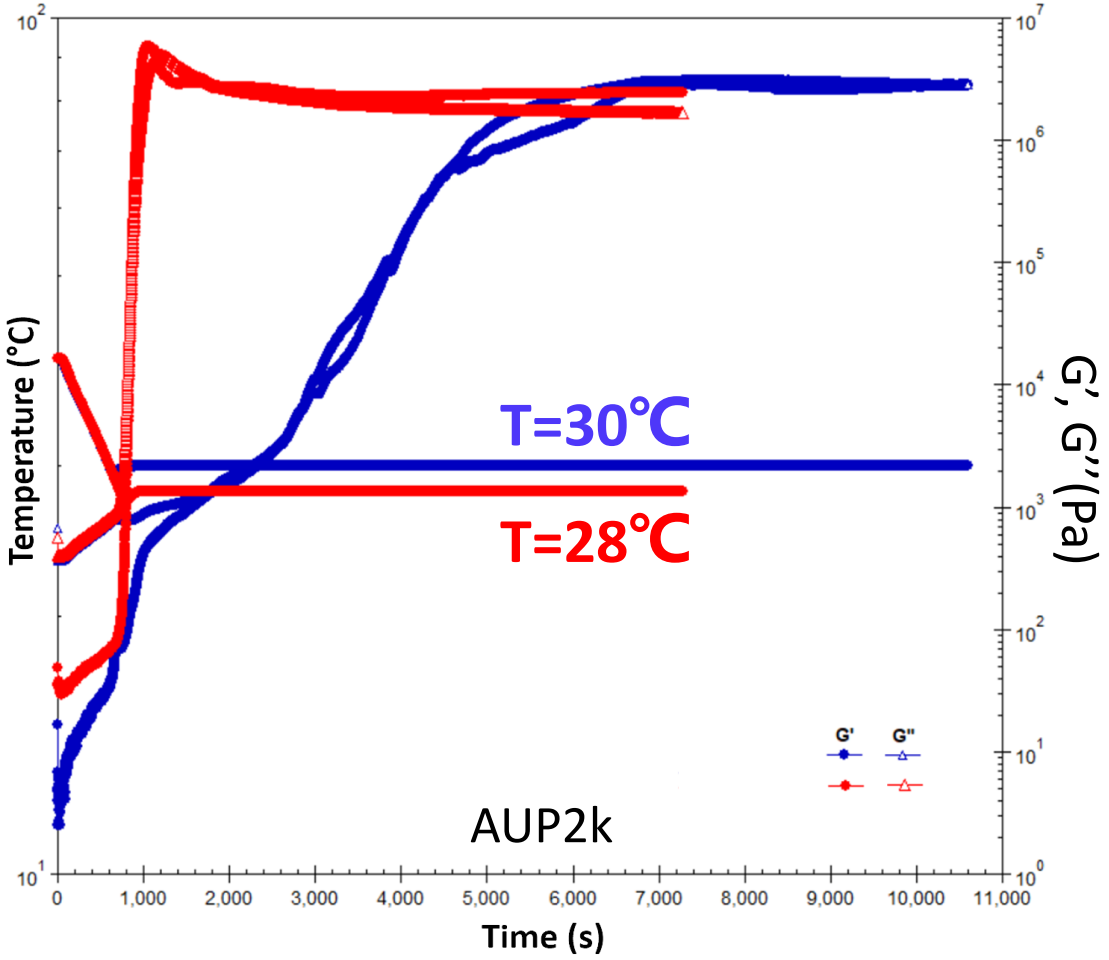
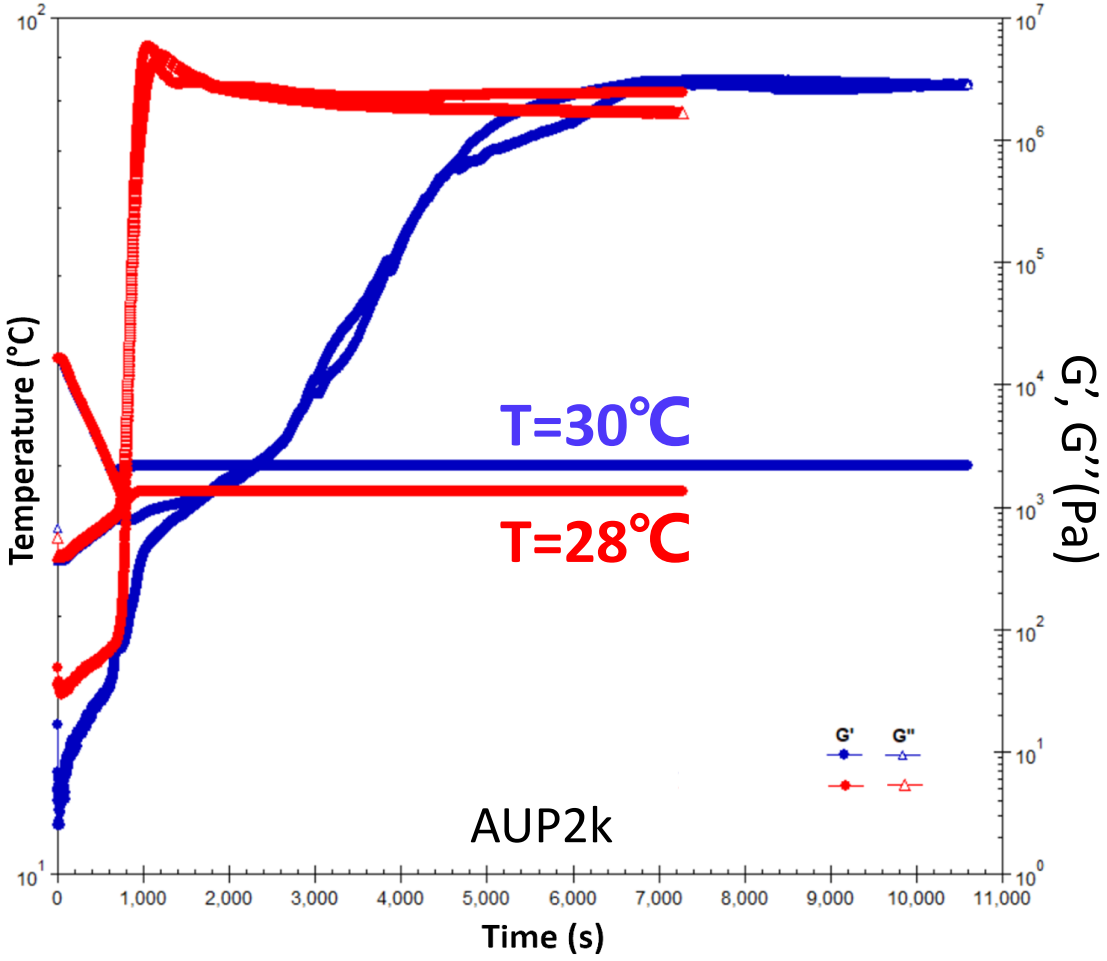




Isothermal-crystallization: the equilibrium state is rapidly reached at lower temperature.



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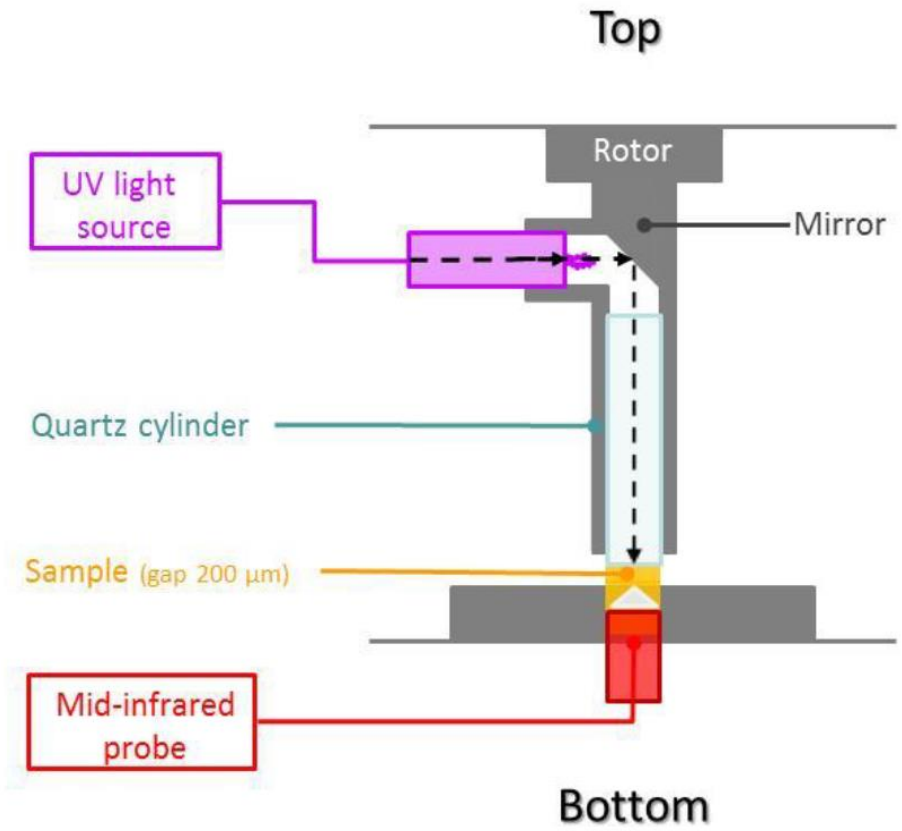
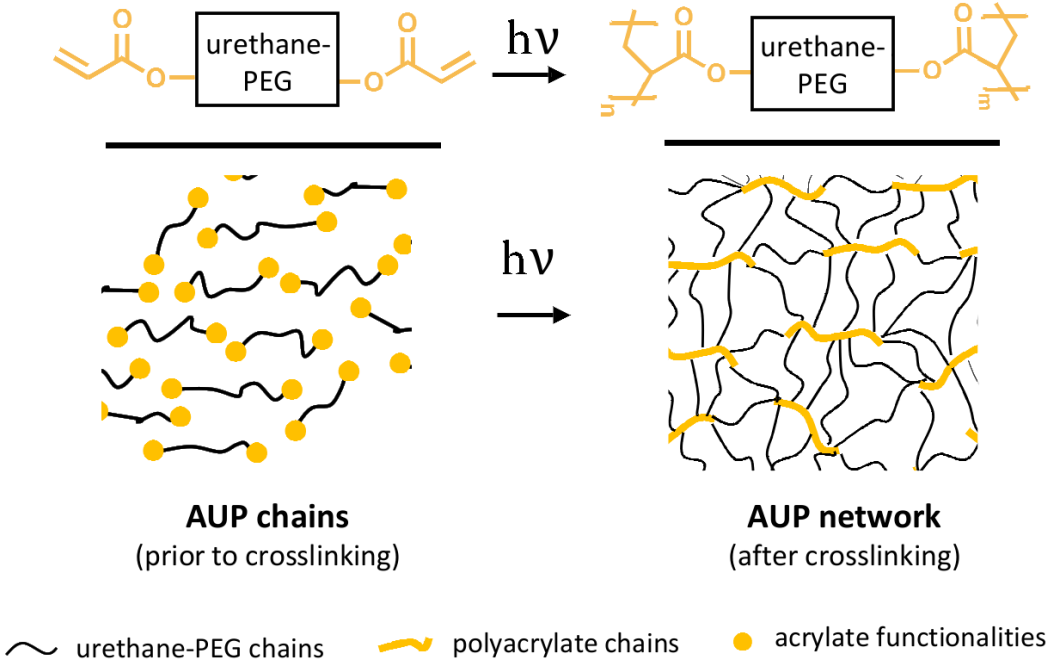
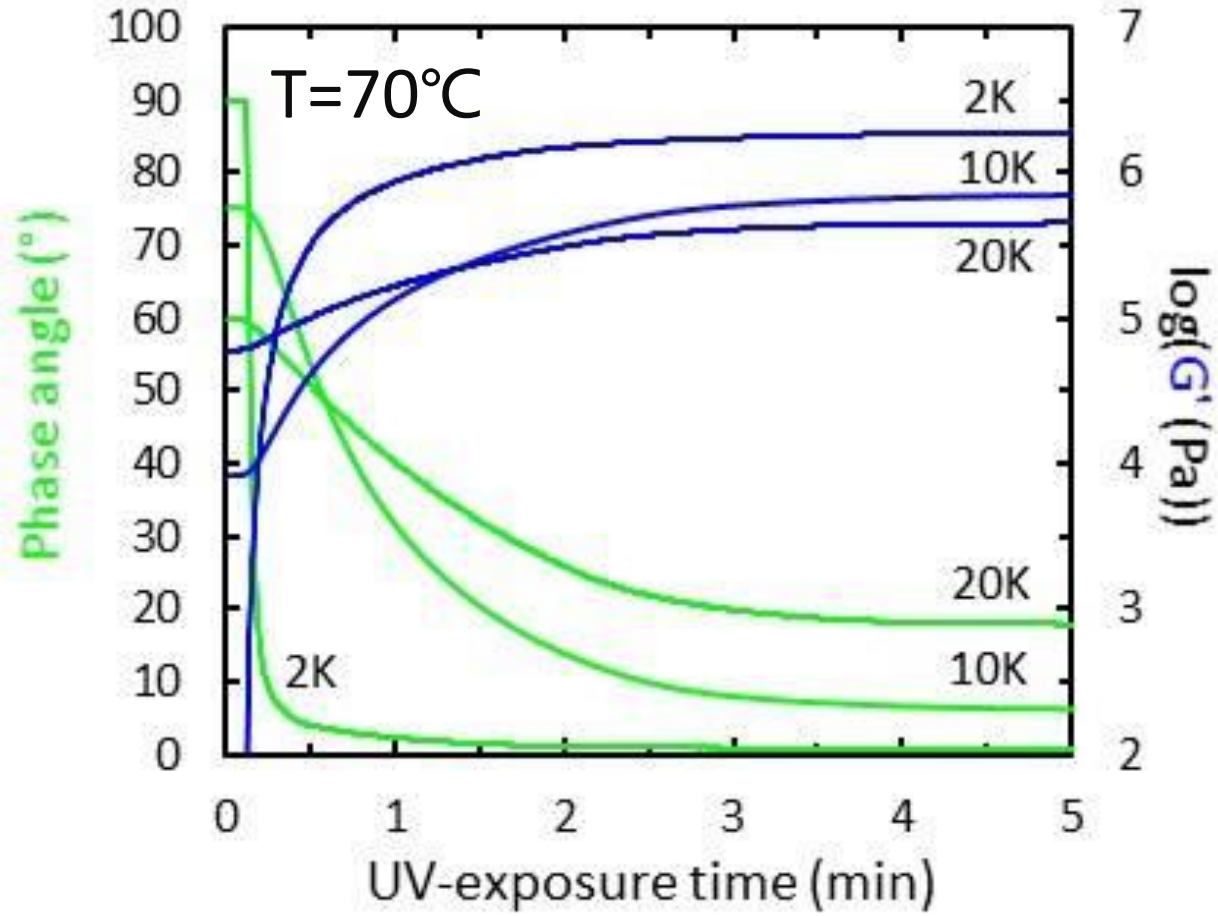


Macromolecules, 2018, 51(14), 5027–5038.

UV Photo-crosslinking on rheometer

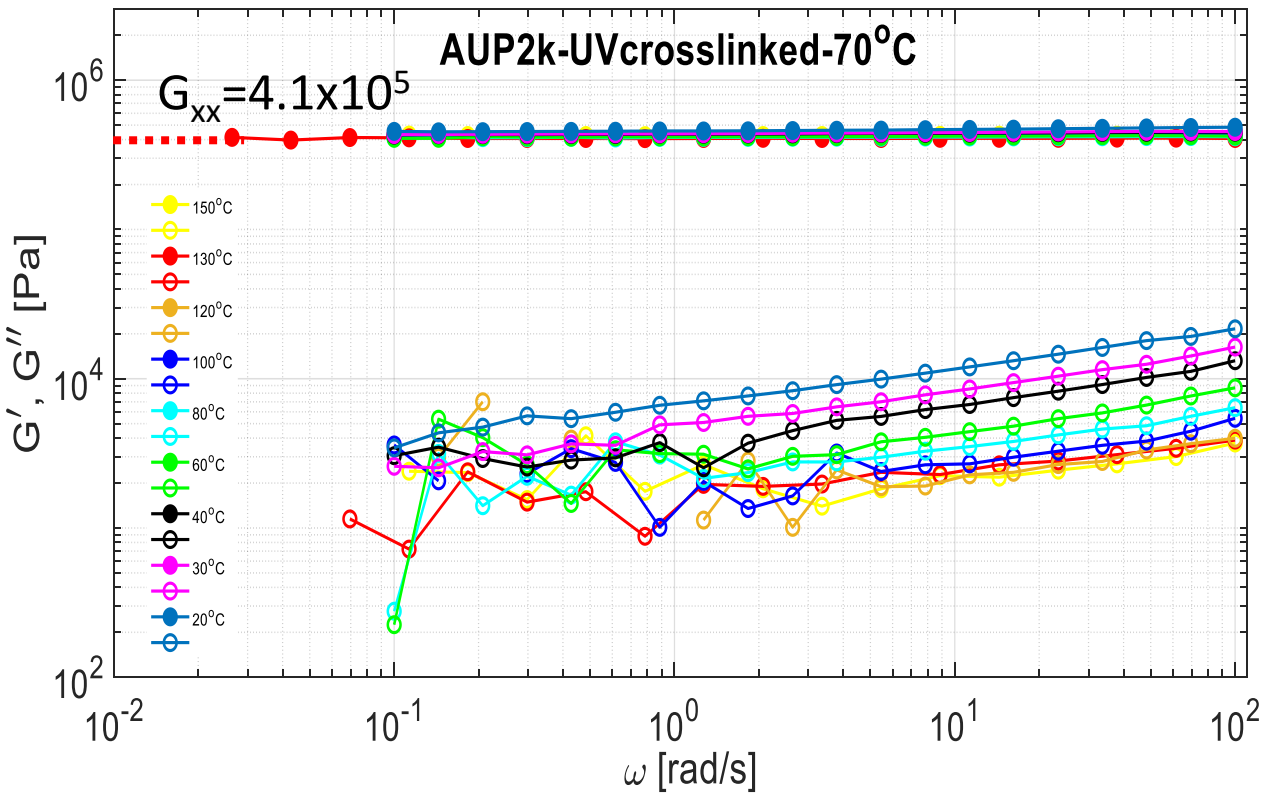


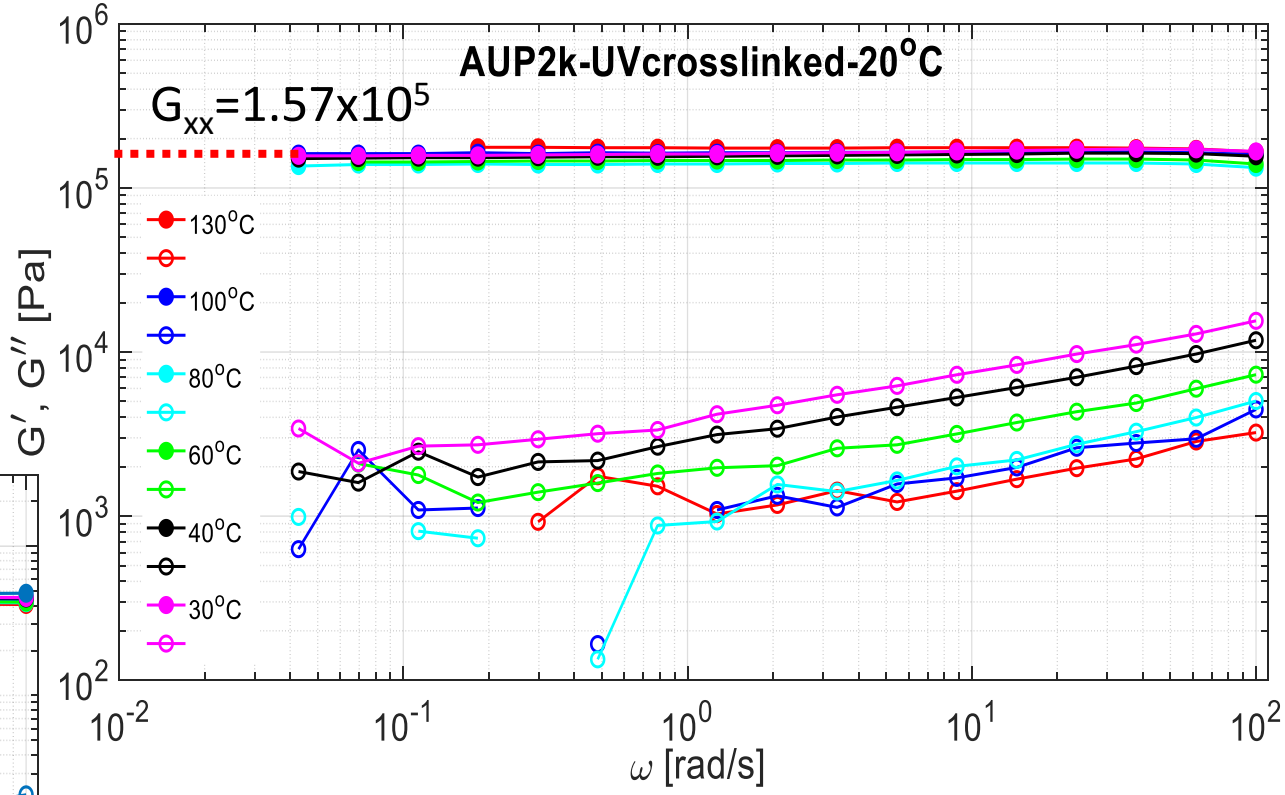


The photo-crosslinking reaction completes in 5mins. The plateau storage modulus decreases with increasing molar mass.

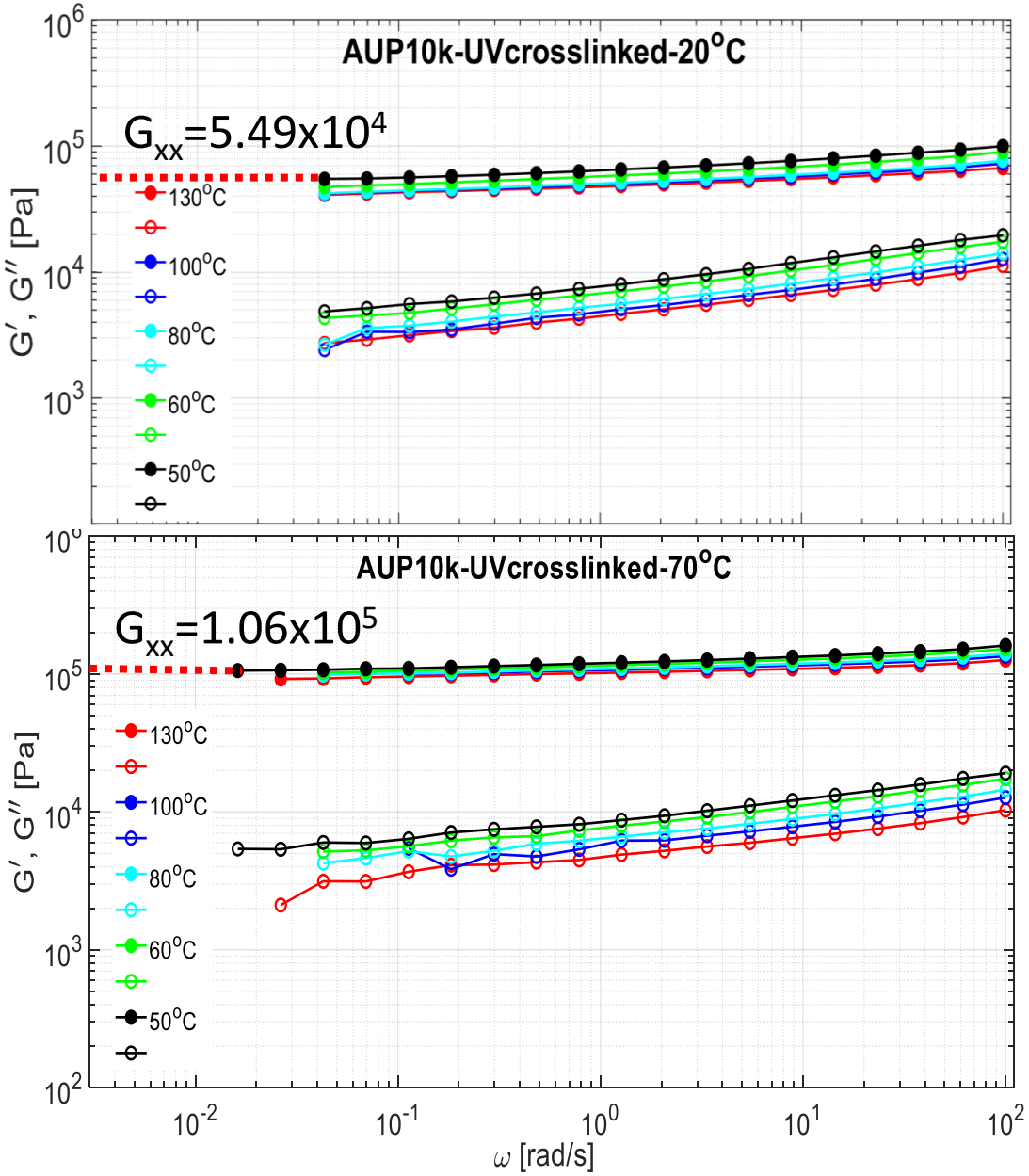
The Influence of Temperature on Photo-crosslinking

A lower chemical crosslinking plateau modulus is observed for AUP2k photo-crosslinked in solid state(20℃).





The Influence of Molar Mass on Photo-crosslinking



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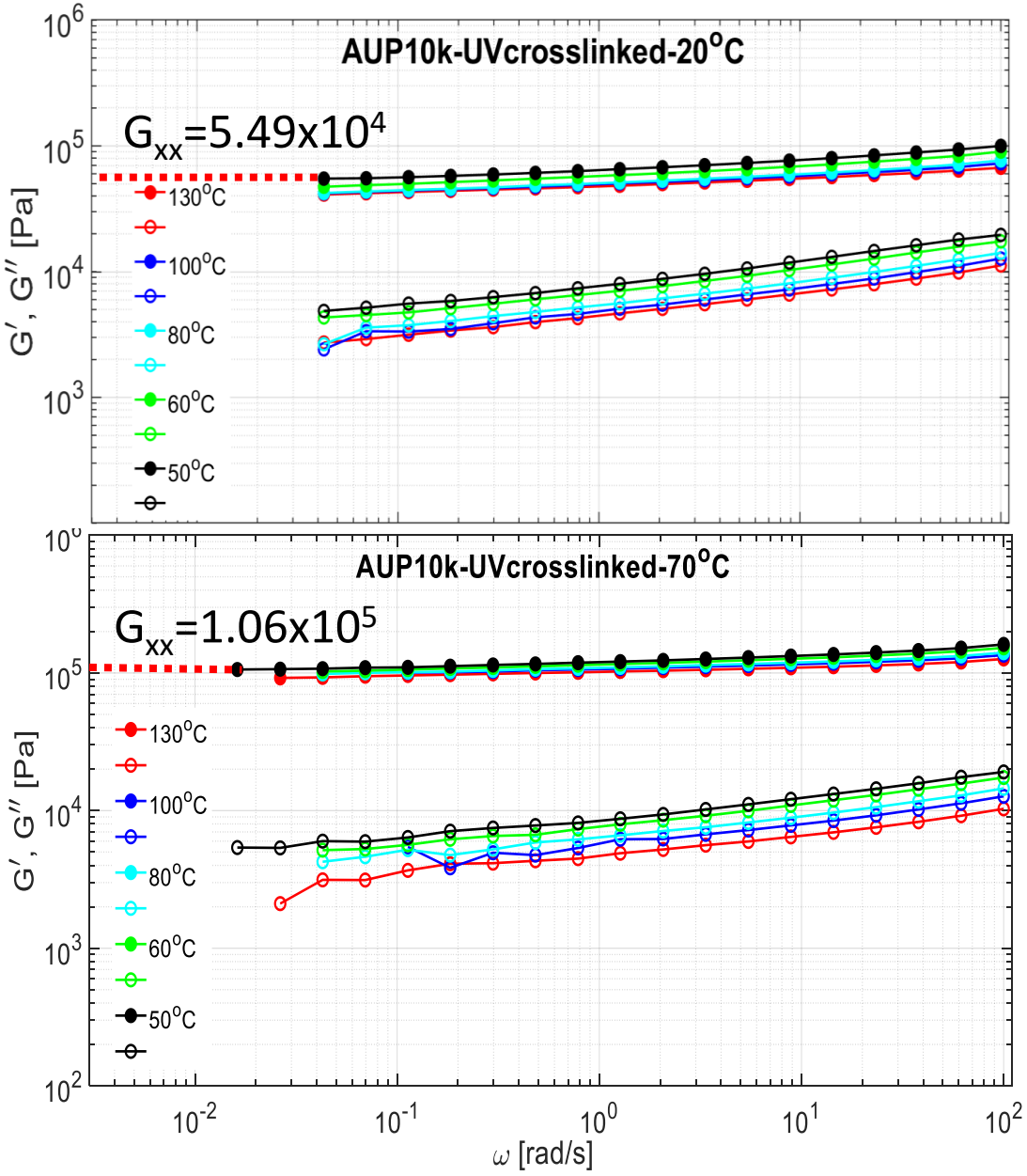
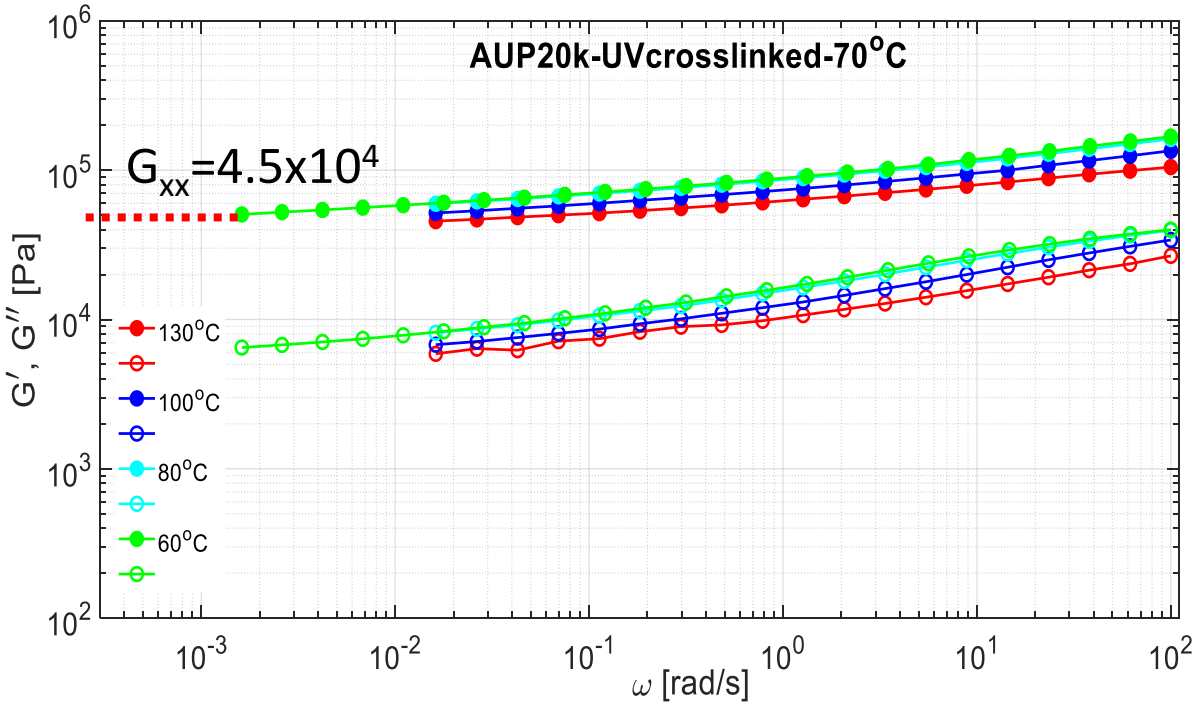
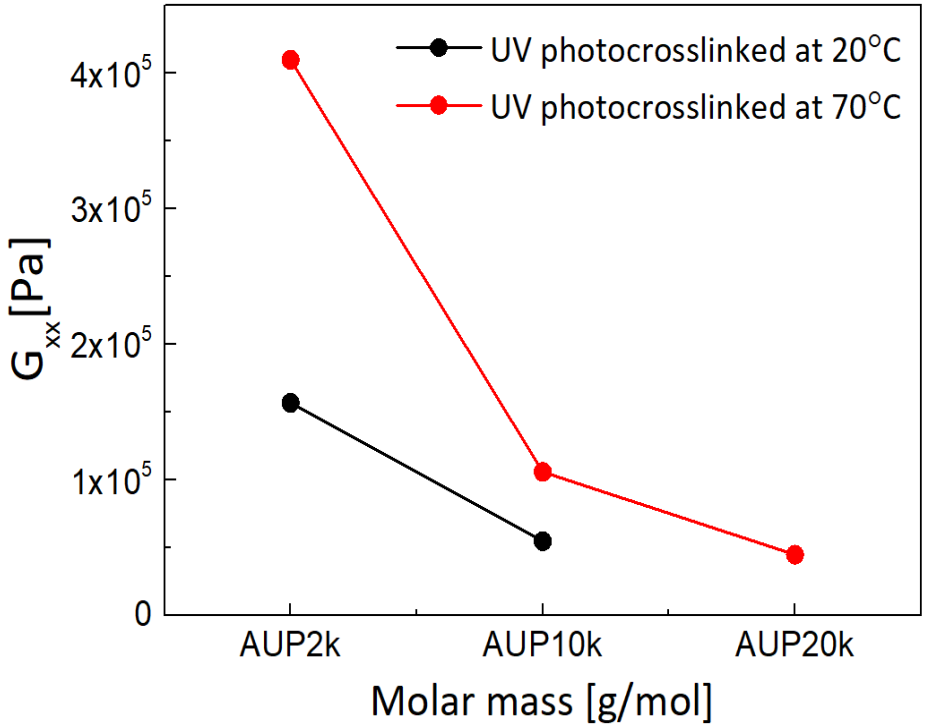
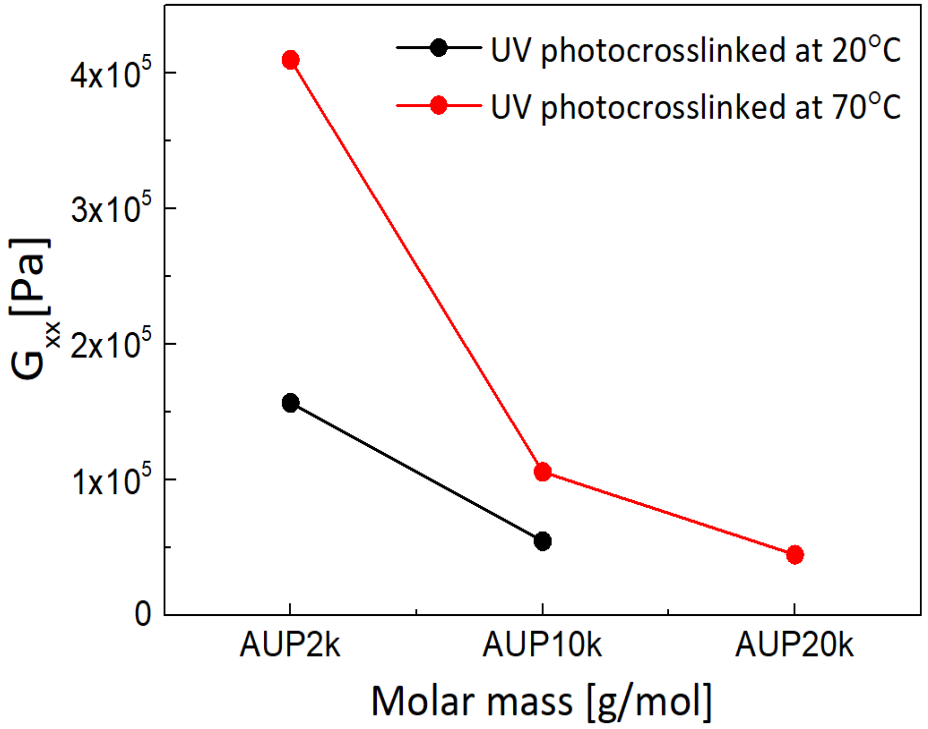
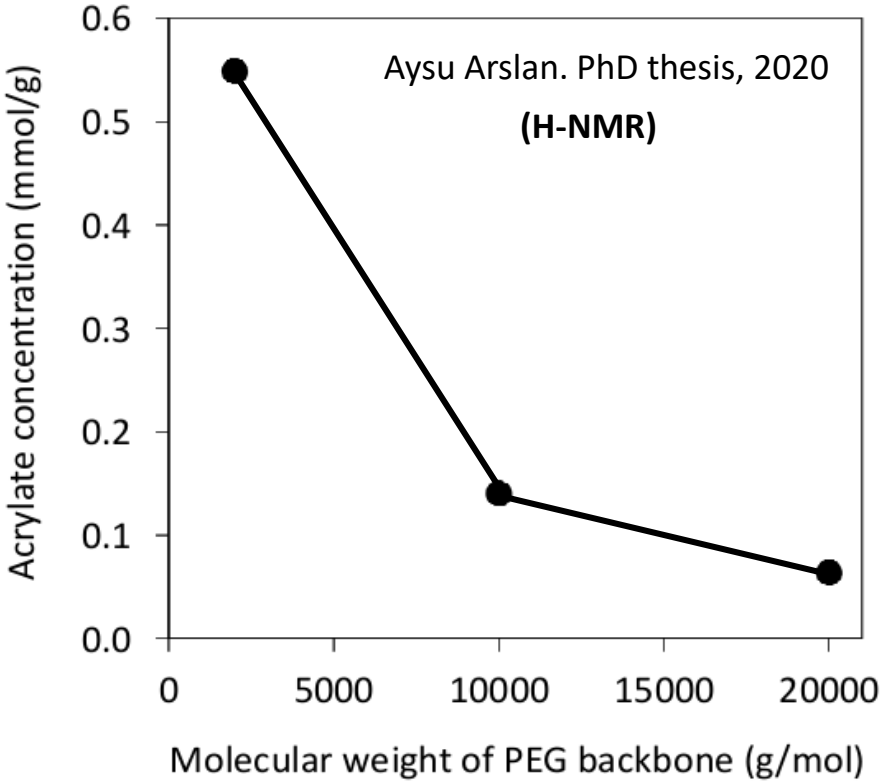


With increasing the molar mass of the backbone, the chemical crosslinking plateau modulus deceases.




UV photocrosslinked at 20°C
UV photocrosslinked at 70°C
4x10^5
3x10^5
2x10^5
1x10^5
0
G_xx [Pa]
AUP2k
AUP10k
AUP20k
Molar mass [g/mol]

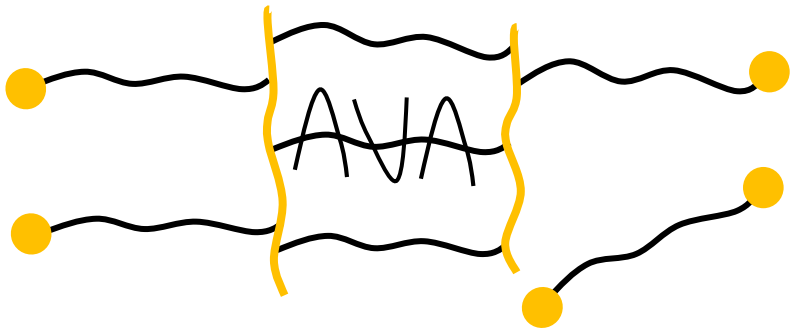




With increasing the molar mass of the backbone, the concentration of the acrylate groups deceases, leading to a low degree of photo-crosslinking reactivity.

The diffusion/mobility of the polymer chain plays an important role in the UV photo-crosslinking reaction.

Crosslinking Density of AUP Networks



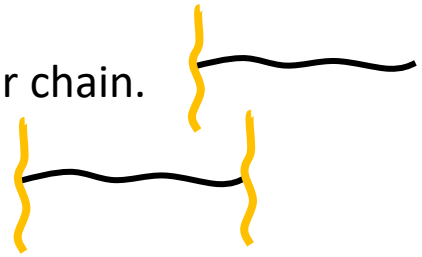
Free polymer chain

Cross-linked at one end of the polymer chain

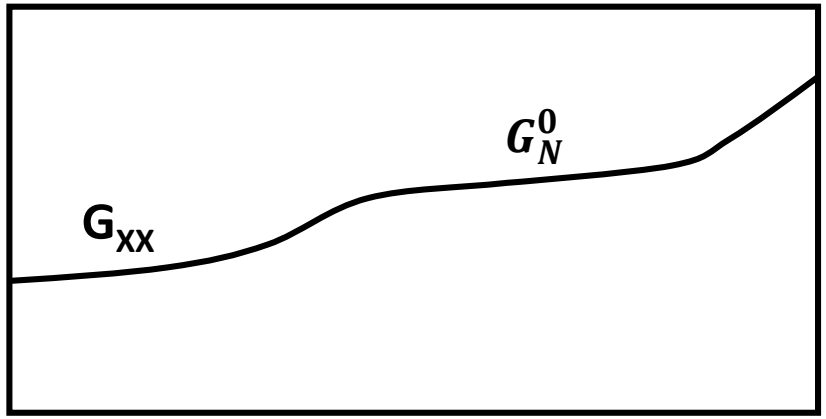
Cross-linked at both of the polymer chain ends

$p_{crosslink}$: the probability that an crosslinking event takes place for an acrylate group.

$2p_{crosslink}(1-p_{crosslink})$: the probability that an crosslinking event takes place at one end of the polymer chain.



$p^2_{crosslink}$: the probability that an crosslinking event takes place at both of the polymer chain ends.

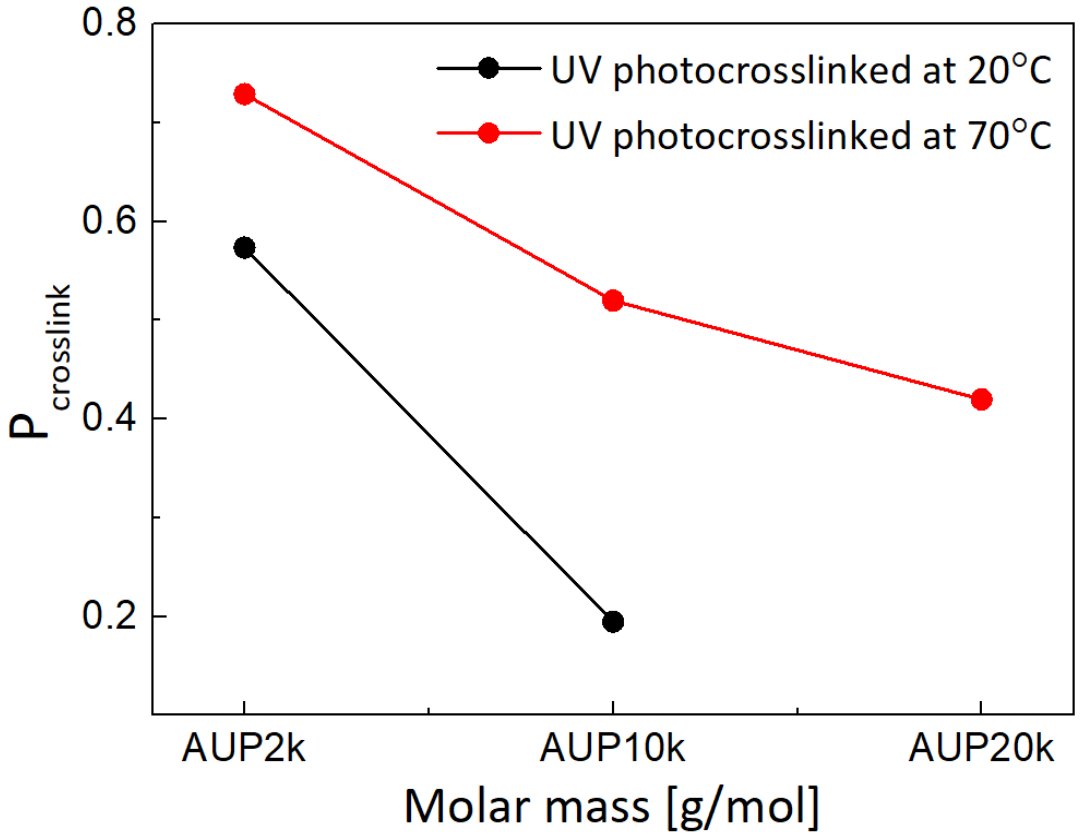


G_N^0 =ρRT/M_e=1.45x10^6 Pa; (M_e=2000 g/mol)

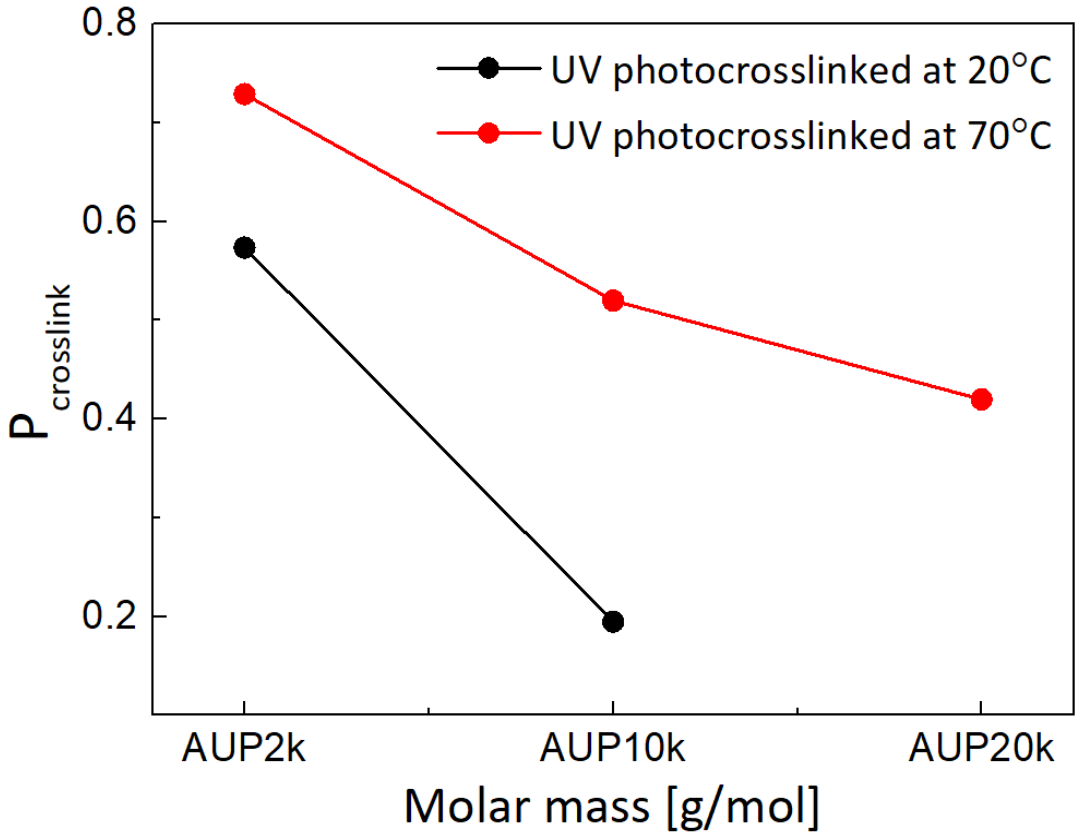
Φ: The weight fraction of the polymer chains, which are cross-linked at both of the chain ends.

$G_{XX} = G_N^0 * \Phi^2$

$\Phi = p^2_{crosslink}$



The photo-crosslinked fraction: $2p_{crosslink}(1-p_{crosslink}) + p_{crosslink}^{2}$



Final conversion of the acrylate group was obtained by differential photocalorimetry (DPC) experiment

Precursor	Physical state	R_{max} (s^{-1})	p_f
AUP2	solid	0.055	0.63
	molten	0.011	0.99
AUP10	solid	0.033	0.64
	molten	0.016	0.68
AUP20	solid	0.009	0.57
	molten	0.005	0.66

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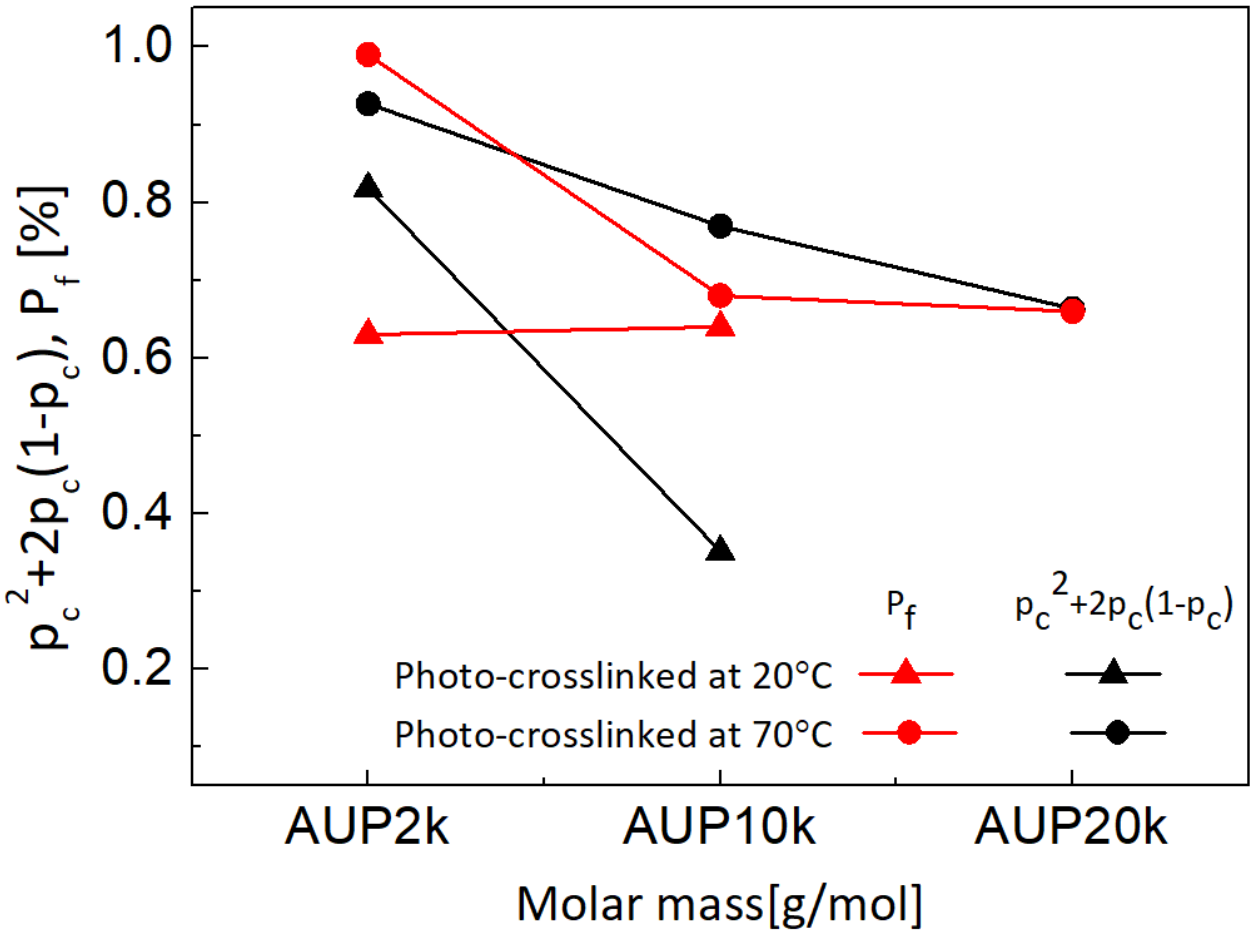
The photo-crosslinked fraction: $2p_{crosslink}(1-p_{crosslink}) + p_{crosslink}^{2}$



Rheology/DPC measurement?

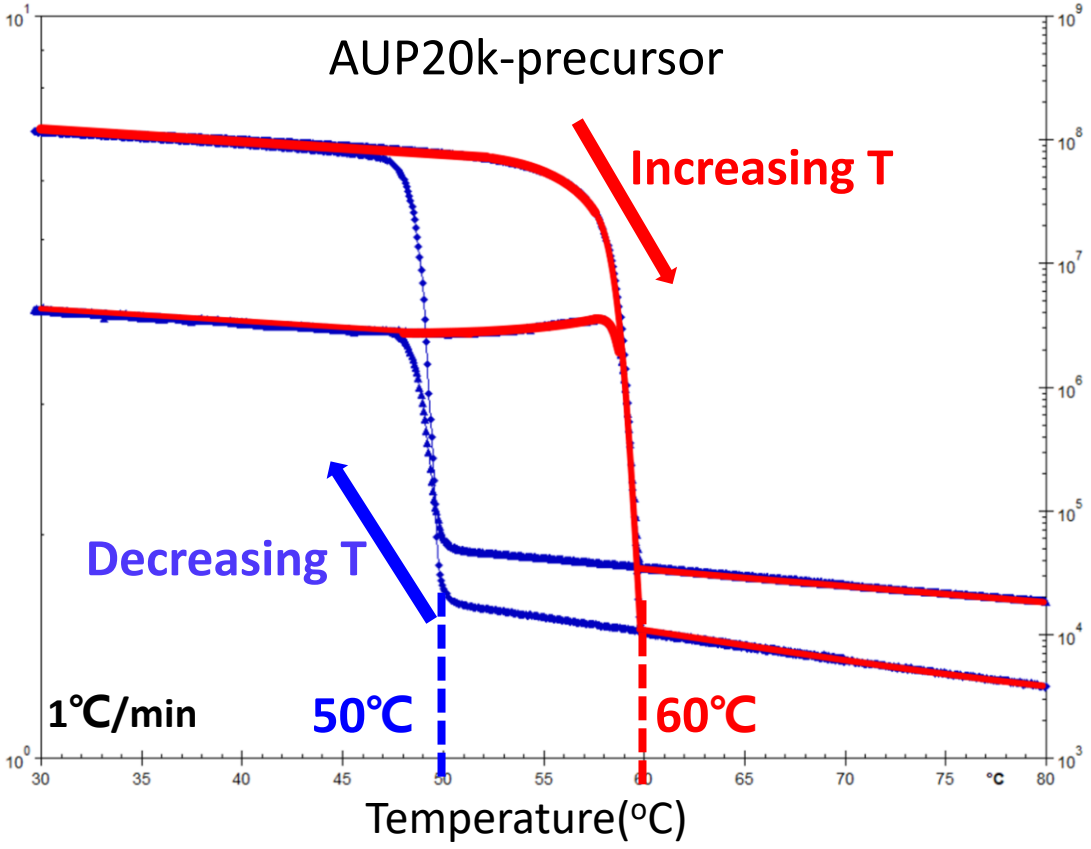
$p_{crosslink}$ in solid state?

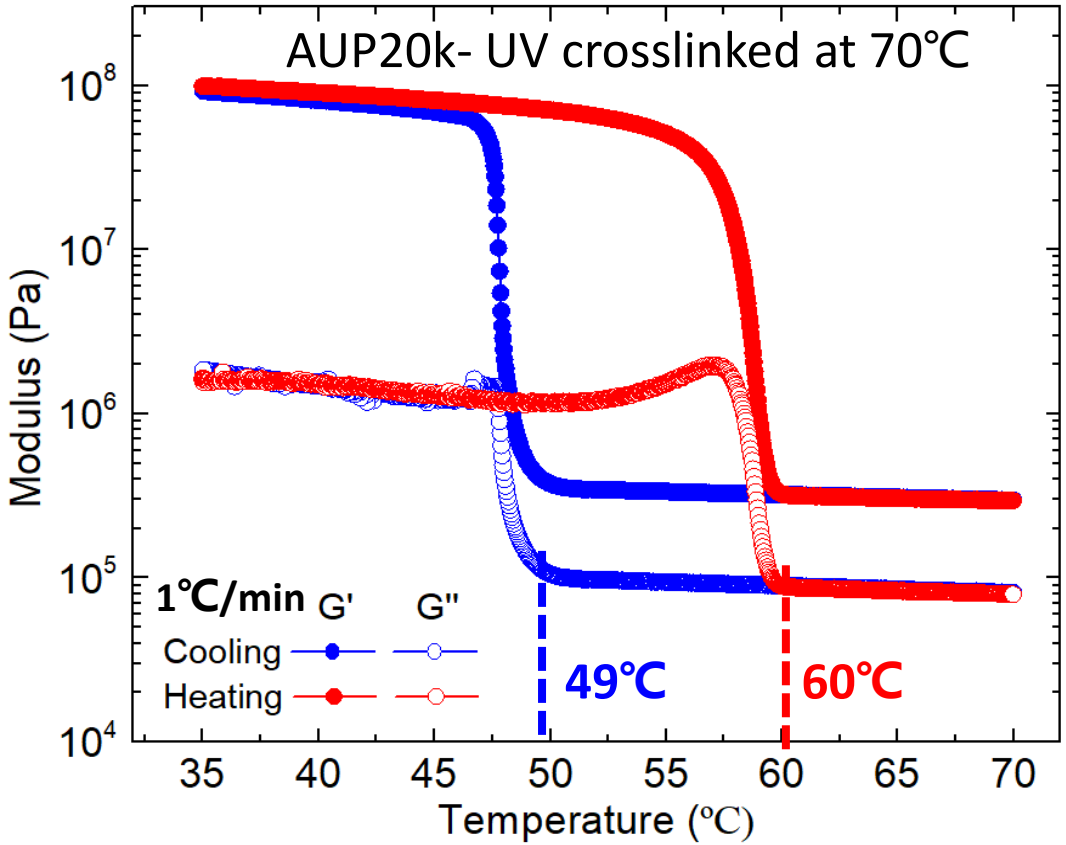
Conclusions and Perspectives

- Photo-crosslinking density in solid state(20°C) is lower than that of the counterparts in molten-state(70°C). With increasing the molar mass of AUPs, the crosslinking density decreases due to lower concentration of acrylate groups.

- The fraction of acrylate groups that is photo-crosslinked was estimated. A good agreement was found in molten state with the one obtained by DPC measurement.

- Further study on these AUP networks in hydrated state will be expected.

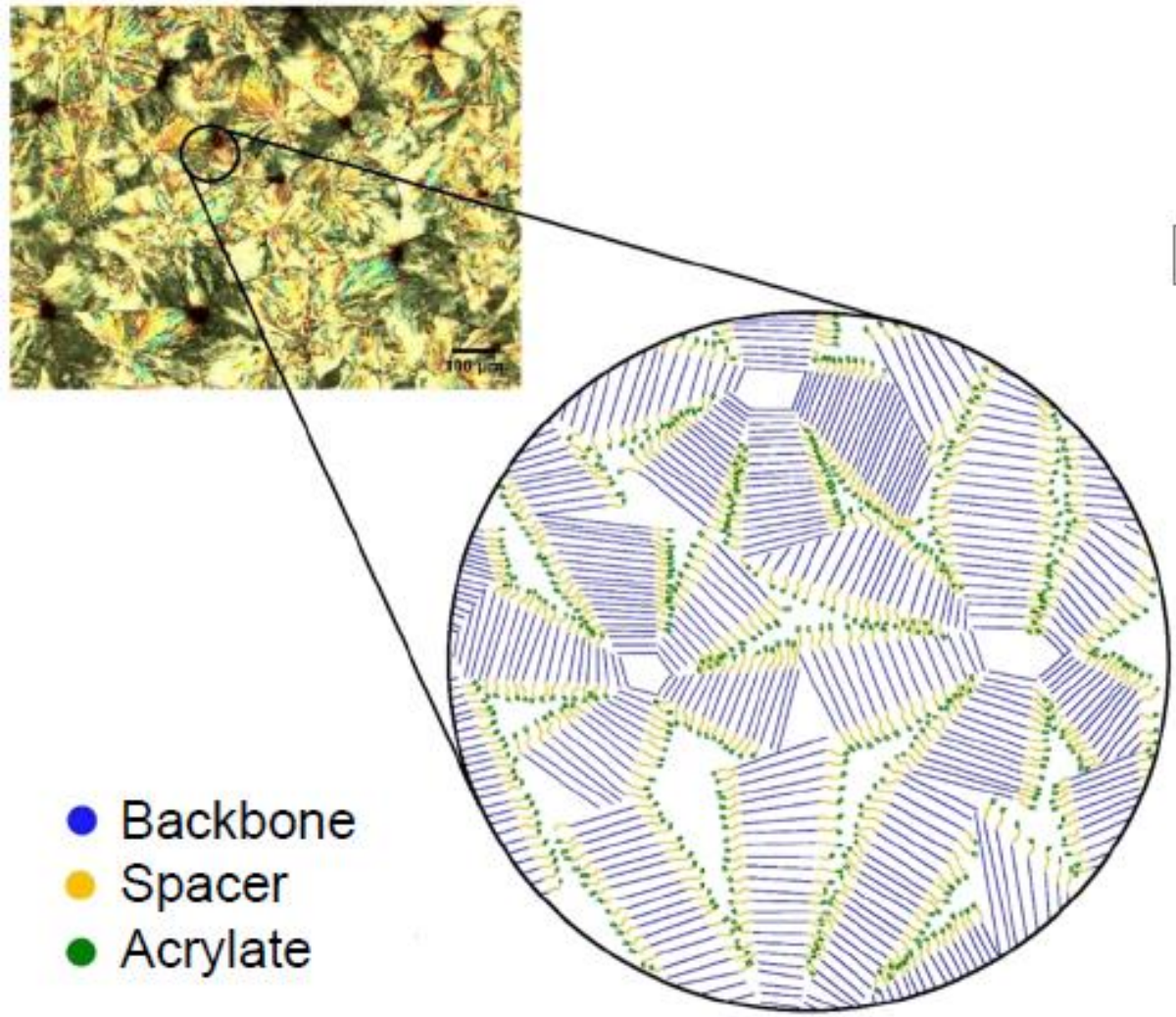




Crystals can be formed for AUP20k precursor and AUP20k-UV crosslinked at 70℃.

AUP2k: If the precursor sample is photo-crosslinked in molten state, the resulting network cannot crystallize anymore? If the precursor sample is photo-crosslinked in solid state, even if the sample is melted, the crystals can be re-formed back once temperature is decreased?

Thank you for your attention.


Backbone
Spacer
Acrylate

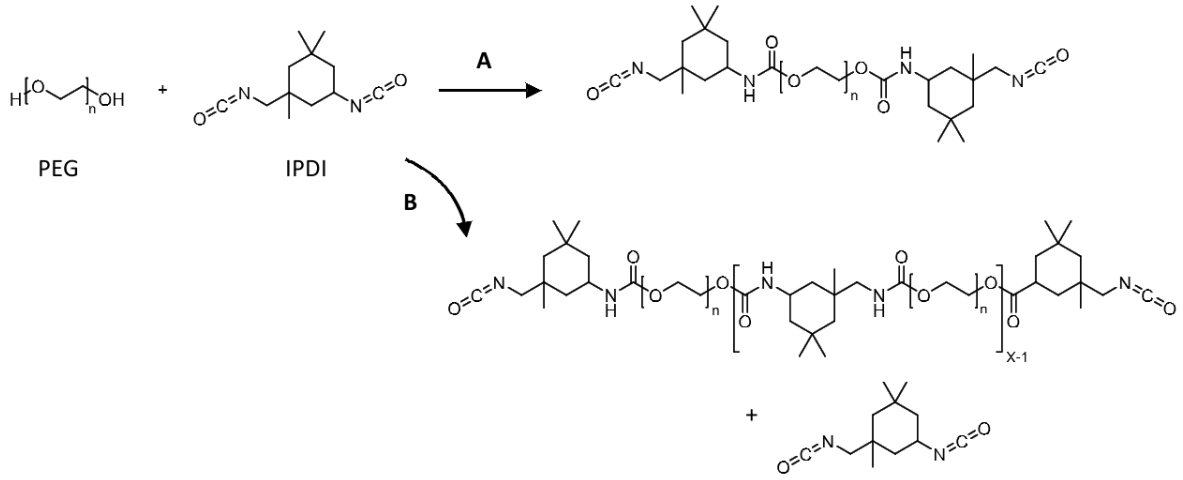


Figure 2.6. The reaction of PEG and IPDI during the 1st reaction step using catalysts of a different selectivity: (A) using a catalyst that is highly selective (e.g. DBTL) over the secondary isocyanates resulting in a monodisperse intermediate product and (B) using a catalyst of a lower selectivity (e.g. Bi neodecanoate), resulting in an intermediate product with "PEG-IPDI" units repeating with an average number of x, and yielding unreacted IPDIs

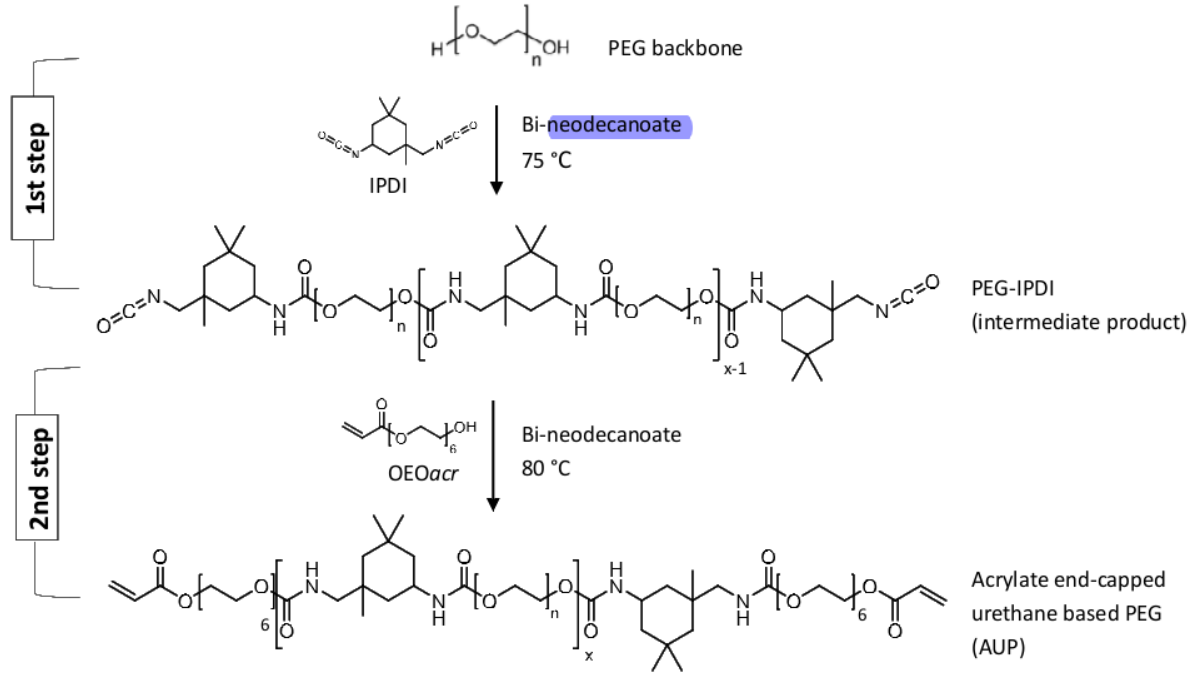
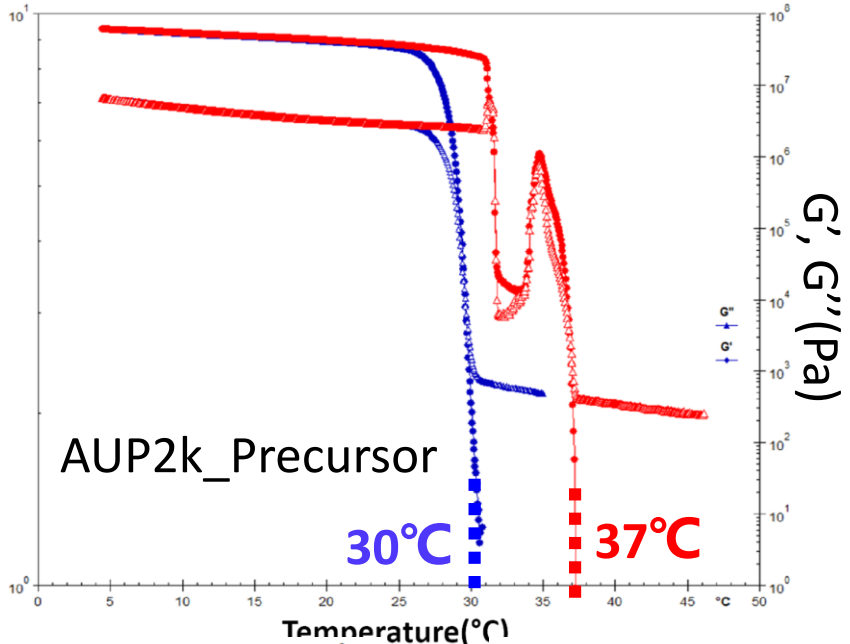
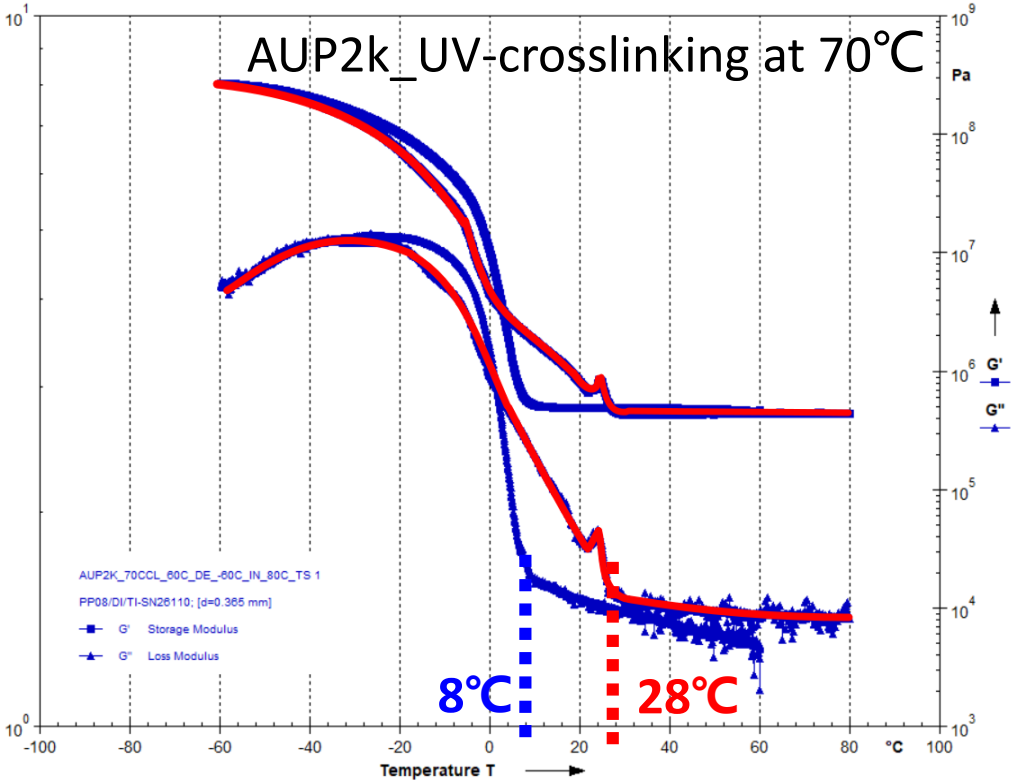
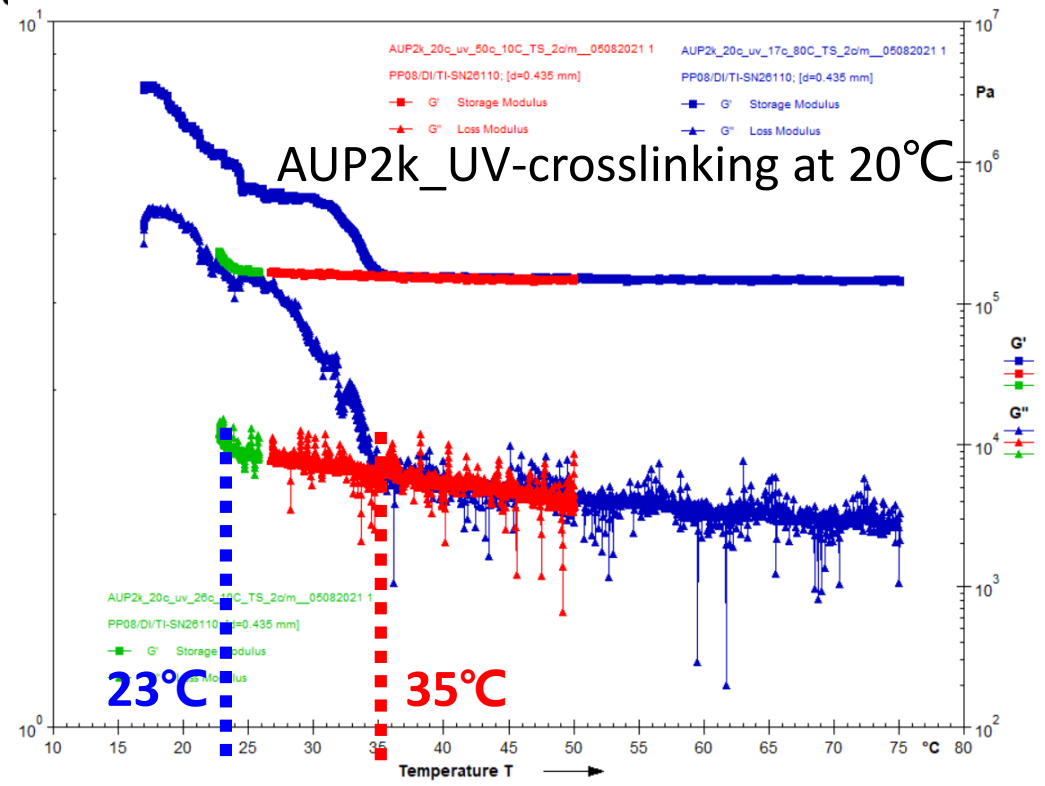


Figure 2.2. Reaction scheme for AUP synthesis

	Molar mass of PEG backbone (g mol^{-1})	C_{acr} (mmol g^{-1})	M_n (g mol^{-1})	M_w (g mol^{-1})	Đ
AUP2	2000	0.550	7400	8900	1.2
AUP4	4000	0.330	9900	14000	1.4
AUP8	8000	0.166	17800	28000	1.6
AUP10	10000	0.141	23000	31300	1.4
AUP20	20000	0.065	39600	63800	1.6


AUP2k_Precursor
30℃
37℃
G', G''(Pa)
Temperature(℃)


AUP2k_UV-crosslinking at 70℃
AUP2K_70CCL_60C_DE_-60C_IN_80C_TS 1
PP08/DI/TI-SN26110; [d=0.365 mm]
G' Storage Modulus
G'' Loss Modulus
8℃
28℃
Pa
G'
G''
Temperature T


AUP2k_UV-crosslinking at 20℃
AUP2k_20c_uv_50c_10C_TS_2c/m__05082021 1
PP08/DI/TI-SN26110; [d=0.435 mm]
G' Storage Modulus
G'' Loss Modulus
AUP2k_20c_uv_17c_80C_TS_2c/m__05082021 1
PP08/DI/TI-SN26110; [d=0.435 mm]
G' Storage Modulus
G'' Loss Modulus
23℃
35℃
Pa
G'
G''
Temperature T