



**Novel polymer conetworks of zwitterionic
2-acrylamido-2-methyl-1-propanesulfonic acid
and poly(ethylene glycol) acrylate macromonomers
with pH and thermally sensitive
swelling behavior**

SSC thesis

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1. INTRODUCTION

Polymer hydrogels are hydrophilic macromolecules, composed of crosslinked polymer chains that extend in all directions of space. Due to their hydrophilic properties, they have a wide range of applications. Since the second half of the 20th century, these materials have gained an increasing importance as medical devices, for example, as contact lenses, superabsorbents in diapers, drug carriers or scaffolds for tissue engineering, etc.

A large group of crosslinked systems are based on poly(ethylene glycol) (PEG). Nowadays, PEG is widely used in many areas of science and our everyday life, due to its special properties. PEG is water soluble and biocompatible, making it suitable for a variety of food industrial and biomedical applications. PEG is a linear polyether and therefore has a maximum of two chain end functional groups. This determines its functionalization, so it can be produced in mono- or bifunctional forms as appropriate. Accordingly, acrylate or methacrylate groups can be formed at one or both ends of the chain. One such polymer, containing a diacrylate group is poly(ethylene glycol) diacrylate (PEGDA), which is a hydrophilic bifunctional polymer and thus suitable for use as a crosslinker. There are also monofunctional PEG derivatives, such as poly(ethylene glycol) acrylate (PEGA), which is a biocompatible, thermoresponsive polymer. Nowadays, there is an increasing number of scientific investigations in which these two materials, mono- and bi-(meth)acrylate-functional PEGs are applied as reactants and components of various macromolecular architectures.

In addition to the above, polymers containing different ionic functional groups are gaining ground. Their great advantage is their ionic nature, which can, for example, influence the water uptake of different hydrogels. Polymer networks made up of polymers with ionic side chains are quite versatile. By varying the amount of the ionic functional groups, for example, the flexibility, swelling, water retention or photosensitivity of the crosslinked polymers can be fine-tuned. They can also be used in specific applications such as biomedical devices, sensors, catalysts and drug carriers.

Taking all these into account, my work aimed at exploring the preparation and properties crosslinked polymers containing 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), an ionic monomer, and mono- and biacrylate functional PEGs. Surprisingly, polymer conetworks with such components belong to a less investigated

class of polyelectrolyte hydrogels, in spite of their low toxicity, and especially the high stability, ionic and antimicrobial properties of the homopolymer and copolymers of AMPS.

2. BACKGROUND, LITERATURE OVERVIEW

2.1. Hydrogels

Crosslinked polymer networks are three-dimensional polymer meshes, structurally connected by physical or chemical lattice points, called crosslinks. This enables them to absorb large amounts of solvents, depending on the properties of the polymer that makes up the crosslinked network. If the crosslinked polymer structure can absorb water, the material is called a hydrogel. If large extent of swelling can be measured in alcohols, it is called an alcogel. If it can take up some other hydrophobic solvent, the swollen material is called an organogel. By definition, gels able to absorb at least 10% of their own mass of water are considered as hydrogels.

The therapeutic application of hydrogels with suitable polymeric structures and the conditions for their use were first mentioned by Witcherle and Lím in 1960, almost half a century after the concept of hydrogels was defined [1]. Hydrogels have similar mechanical properties to tissues that make up certain biological systems due to their high water content. Their hydrophilicity is due to the action of various functional groups linked to the polymer chain, such as -OH, -COOH, -CONH, -CONH₂, -NH₂, -HSO₃ [2].

Five types of hydrogels exist: homopolymer and copolymer networks, semi-interpenetrating networks (semi-IPN), interpenetrating networks (IPN), and conetworks.

Homopolymer networks contain only one type of monomer, whereas copolymer networks contain two or more types of monomers which are crosslinked [3-5].

Semi-IPNs are produced when one or more types of linear, or branched polymers are incorporated into the polymer chains of a crosslinked polymer without forming chemical bonds. The advantage of these systems is that they are able to behave accordingly to the structure of the two types of polymers, without the formation of chemical bonds, for example by changing their properties in response to changes in temperature or pH [6].

IPNs are macromolecular substances in which at least two crosslinked networks are incorporated in each other, but without anychemical bond between the two polymer networks. This can be produced by crosslinking a different monomer between the lattice points of an already available crosslinked polymer [7].

Polymer conetworks consist of different polymer chains interconnected to each other by chemical bonds. Usually, one of the polymer chains is a macromolecular crosslinker for the other polymer.

The starting materials for hydrogels are often monomers with a (meth)acrylate group, for example mono(meth)acrylates, (meth)acrylic acid and its salts, or various (meth)acrylamides. The most common crosslinkers are various small molecule di(meth)acrylates and amides, and various bifunctional polymers. Ethylene glycol dimethacrylate (EGDMA) and its poly(ethylene glycol)-based analogues are very common [8].

2.2. Poly(ethylene glycol) based hydrogels

Poly(ethylene glycol) (PEG) is a polyether macromolecule, obtained by a ring-opening polymerisation of ethylene oxide, is a widely used and well-known water-soluble polymer, the structure of which is shown in **Figure 1**.

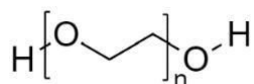


Figure 1: *Structural formula of poly(ethylene glycol) (PEG)*

As already mentioned in subsection 2.1, mono- and di(meth)acrylate derivatives of PEG are the basis of numerous hydrogels. Examples of such (meth)acrylates are PEGA, PEGDA, PEGMA and PEGDMA, which are shown in **Figure 2**. The importance and prevalence of these functional PEG derivatives are illustrated by the fact that a number of analogues of both mono- and bifunctional PEG derivatives of different molecular weights are commercially available from a number of chemical manufacturers and distributors.

The monofunctional acrylates are used as comonomers to affect the properties of polymer networks, and the bifunctional acrylates and methacrylates are commonly used as hydrophilic, biocompatible crosslinkers.

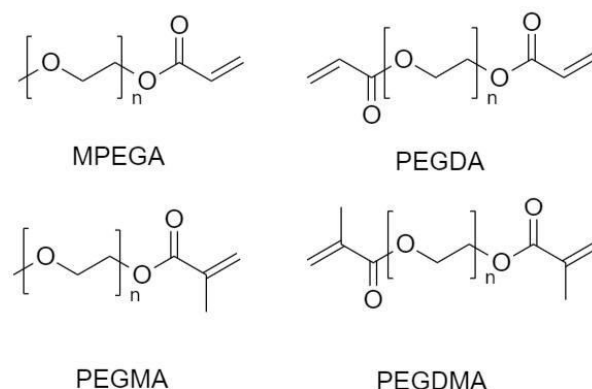


Figure 2: Structural formulae of methoxy PEG acrylate (MPEGA), PEG diacrylate (PEGDA), PEG methacrylate (PEGMA), PEG dimethacrylate (PEGDMA)

Nowadays, intensive research is being carried out in many areas on the use of PEGs due to their biocompatibility, which allows their use in biomedical fields. They are non-toxic and their physical properties are very similar to those of living cells and tissues due to their water content. In addition to their biomedical applications, they are of outstanding importance in many other fields. PEG hydrogels are used in microbiology as a virus concentrating agent, surfactant in detergents, additive in various cosmetic products, or emulsifier in toothpastes [9].

Among the applications and research areas, the study of pH-sensitive networks have a major focus. The side chains of pH-sensitive polymers contain at least one functional group that is capable of protonation as well as deprotonation depending on the pH. These properties of PEG-based hydrogels have been investigated, for example, using silver nanoparticles. Poly(2-hydroxyethyl methacrylate) (PHEMA), PEGMA and methacrylic acid (MAA) were used to form the meshes. In this study, Ag^+ ions bound to hydrogels were reduced using deprotonated carboxylic acid groups. The size and morphology of the reduced silver nanoparticles in the composite hydrogels could be varied by the amount of water the hydrogels contained while the nanoparticles were being released to their surface. In addition, the silver-ion-bound networks produced much higher swelling degrees and water release rates than their silver-free counterparts. Their applications are mainly in electronic devices, biosensors and drug delivery [10].

It was mentioned earlier that PEG is biocompatible and tissue friendly. Therefore, tissue engineering, drug delivery and peptide stabilization are also prominent areas of research. Drug delivery requires that the hydrogel has a porous structure, for example a large internal surface area. Such porous structures can be

produced by controlling two conditions: the proportion of crosslinkers in the system and the amount of hydrophilic components that control the rate of aqueous swelling. The main advantage of these crosslinked networks is the prolonged release of the active ingredient, which is controllable, uniform and sustainable over a long period of time. Functional groups can be added as well, which can advantageously delay the release of the active ingredient. This is very useful because this delay can protect the drug from an environment that in itself would break it down too early. In addition, degradation can be triggered by pH changes, temperature changes, physical stresses or the presence of enzymes [11].

There are a very large number of publications in the literature using PEG-based hydrogels as drug delivery systems. Among these, I would like to highlight some examples.

First, I would pose poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA)-PEGMA as an example. It produces a very favourable, pH-sensitive, blood-compatible material with a 30/70 mixture and releases insulin at physiological pH in the human body [12].

Delayed-release dendrimer hydrogels have also been developed, for example, for the delivery of anti-cataract drugs, made from poly(amidoamine) G3.0 dendrimer and PEGA. Holden and their colleagues found that the hydrogels are highly bound to mucin and mucous membranes and are non-toxic to human corneal cells. The drug delivery took nearly 72 hours and was much more effective than any eye drops used nowadays [13]. Another scientific publication reports on hydrogels with high mechanical robustness, that can be built in-situ from eight PEG-*b*-poly(lactic acid) acrylates and PEG-thiols, and that it can be designed to degrade and deliver the drug in a predictable manner [14]. Another prominent group of biomedical materials are hydrogels used in tissue culture. Tissue culture processes require hydrogels with structures and properties that can be used as substitutes for different cells. Hydrogels are particularly good materials for this purpose because their structure is very similar to the extracellular matrix of many tissues, they are easy to process and their delivery to the desired site does not require extensive intervention in the human body [15].

Each of these hydrogels is structured according to different criteria, be it physical property, mechanical property, mass transport property or biological property, depending on the target tissue. Synthetic and natural materials can be used in these hydrogel structures, but the prevalence of synthetic materials is

unquestionable, due to their ease of handling, easily modifiable properties and lower cost [16].

Hydrogels are used in three main areas in tissue engineering: they can be space fillers, transport bioactive molecules or be used as building blocks to construct 3D structures in tissues. Site fillers are structures that help to increase size and either inhibit adhesion between tissues or act as bioadhesives [17]. I should point out that PEG itself is also used as an anti-caking agent after surgery [18,19].

As a second use, hydrogels can deliver specific bioactive molecules to target tissues. Nowadays, the most common use is in the direct application of active substances, where they degrade prematurely or do not act in the desired tissues. For these reasons, the highest possible dose is recommended. To avoid high doses, which often unnecessarily burden the body and lead to undesirable side effects, it is advisable to use a molecular transport device that delivers the bioactive molecules to the desired site in the body. There are many examples of this type of substance in the literature, for example, alginate or glutaraldehyde-containing hydrogels with ionic crosslinking [20,21]. Gasperin-Bulbarela and coworkers have demonstrated that not only active substances but also proteins can be bound to hydrogels. These results suggest that PEG-based hydrogels can efficiently transport and deliver not only small drug substances but also macromolecules [22].

The third tissue culture use is due to the 3D structure and high water content of the polymers. They can transmit chemical and mechanical signals and provide an environment for cells to attach, divide or differentiate. These 3D structures can now mimic various tissues, such as cartilage tissue, bone tissue, muscle tissue, adipose tissue and neurons [23-25].

Tissue mimicry is not limited to the skeleton of a living organism (cartilage tissue, bone tissue, muscle tissue). An example of this is the PHEMA-PEGMA-graphene oxide crosslinking, which has been used to make the hydrogel behave in a similar way to liver tissue. The tested network exhibited an increasing degree of swelling in proportion to the amount of graphene oxide incorporated, as well as a high degree of red blood cell compatibility and anticoagulation, for example it prevented platelets from clumping together. In addition, it has been demonstrated that the tested crosslinking was also able to deliver a programmable and long-lasting drug release [26].

In another study, two methacrylate-based monomers, PEGMA and 2-methacryloyl oxyethyl phosphorylcholine (MPC), were incorporated into tetraethylene

glycol diacrylate (TEGDA)-PHEMA networks with different compositions. They found that the surface hydrophilicity of the hydrogels was significantly increased and significant protein adsorption was observed. This behaviour may make it suitable to provide a biocompatible protective coating for various implants and biochips [27].

Another major group of applications are biosensors, which are derived from a combination of physical and chemical sensors. A biosensor is a device that detects and reports the biophysical properties of a system in its environment and collects data about it. An important criteria for any biosensor is that it must have a component that is sensitive to and can analyse biological changes in its environment. The components sensitive to biological activity may be enzymes, antibodies, living cells or tissues, the aim in all cases being to provide a specific response signal for the biological characteristic of interest [28,29]. A good example of the application of PEG in biosensors is the immobilization of oxidoreductase enzymes in a PEG-based crosslinked matrix. The investigated network was HEMA-PEGMA-tris(hydroxymethyl) methyl acrylamide (HMMA) - tetra(ethylene glycol) diacrylate (HEMA-PEGMA-HMMA-TEGDA), which bound ferrocene monocarboxylic acid (FcCOOH). The rate of FcCOOH release was in direct proportion to the wt% of the TEGDA in the hydrogel [30].

In addition, there is significant research about the use of functional PEGs in the development of contact lenses. The hydrogels used in the manufacture of contact lenses have a good adaptability to the physiological state of the desired area. These conditions are generally adequate water content, good mechanical properties, oxygen permeability, surface wettability, good refractive index and translucency, high stability against hydrolysis, easy sterilisation, non-toxicity and biological tolerance to living cells [31]. The vast majority of commercially available contact lenses are based on silicone and HEMA, and their properties can be varied by incorporating different polymers and monomers. One such newly developed contact lens material is a PHEMA - PEGMA - poly(dimethylsiloxane) dialkanol - isophorone diisocyanate multicomponent hydrogel (PHEMA-PEGMA-PDMS-IPDI) [32].

affect the parameters of cell migration, with a much higher number of cells moving in parallel to the hydrogel, adhering to the support structure, than away from the structure [35]. In another interesting study, dye-mixed bovine serum, proteolytically activated fluorogenic substrate was bound to PEG polymer by conjugated bonds and then gel-coated by photopolymerization. The resulting hydrogels could act as cell adhesives. The dyed bovine serum significantly increased the fluorescence of the hydrogel when placed in an enzyme-loaded medium. Fluorescence was used to track cell migration and to observe the proteolytic behaviour of cells. This process was most concentrated at the cell surface and persisted during cell migration [36].

In addition to this, PEGDA-MPEGA space-fillers are also used in tissue culture, as they adhere well to living tissues under high mechanical stress. In addition, they also play an important role in wound treatment, as drug delivery carriers and as coatings for biomedical devices [37,38]. PEG-based hydrogels thus offer a wide range of possibilities for the production of special materials. By incorporating different peptides, forming composites, modifying crosslinks, using fluorescent groups, adding functional groups, incorporating different polymer chains, the properties of PEG-containing hydrogels can be controlled with great variety.

2.4. Ionic monomers in hydrogels

The ionic monomers can promote the hydrophilic nature of the hydrogel, determine the degree of water absorption of the crosslink and make it pH sensitive. A growing number of novel ionic monomers, so-called ionomers are reported in the literature. Examples of such monomers are 2-methacryloyl oxyethylphosphorylcholine, [2-(methacryloyl oxyethyl)] dimethyl (3-sulfopropyl) ammonium hydroxide, or bis-(2-methacryloyloxy)ethyl phosphate, which can be used to modify the properties described above [39-41]. The structure of these molecules is shown in **Figure 4**.

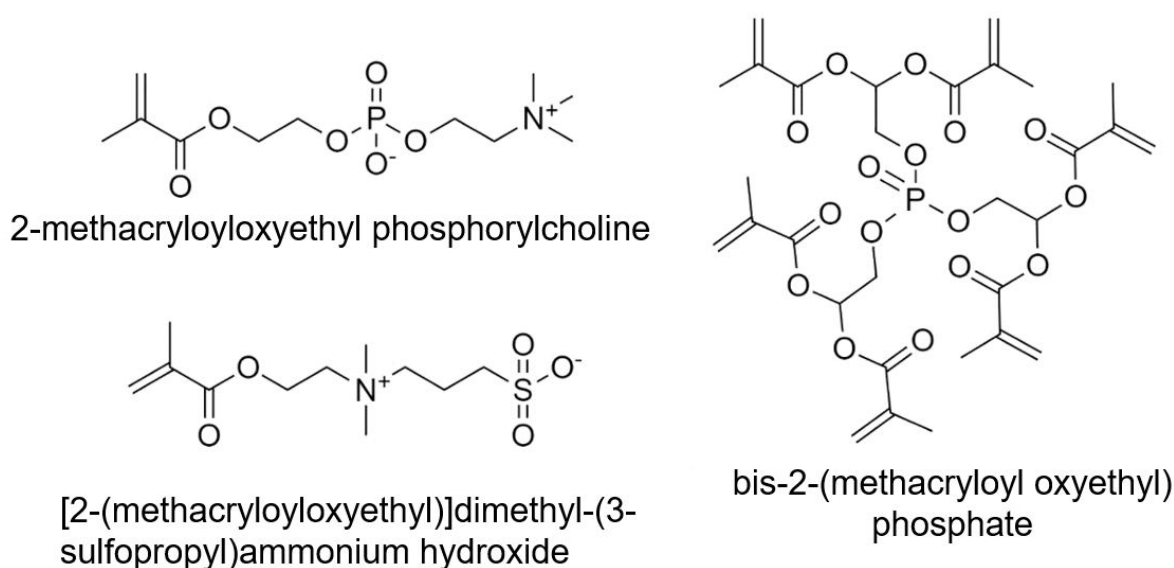


Figure 4: Examples of ionic monomers used in hydrogels

2.5. Hydrogels containing 2-acrylamido-2-methyl-1-propanesulfonic acid

2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is a type of ionic monomer containing a sulfate group. When incorporated into hydrogels, it significantly increases their water absorption and water retention properties. Its structure is illustrated in **Figure 5**.

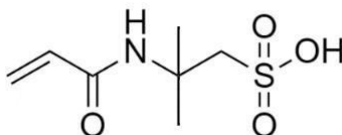


Figure 5: Structural formula of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)

AMPS has very valuable and interesting properties both as a homopolymer and as a copolymer. In the following, I would like to describe some of the studies on AMPS-containing hydrogels that I consider important.

Clara and co-workers have prepared AMPS-methacrylic acid copolymer containing networks using ethylene glycol dimethacrylate (EGDMA) and methylene bis-acrylamide (MBA), where the pH-sensitive nature of AMPS was demonstrated. In the study, it was discovered that hydrogels synthesized with the EGDMA crosslinker exhibit a much higher degree of swelling than the MBA crosslinker but the mechanical stability of the latter was much greater. And due to the AMPS content, the nets showed significant swelling not only in pure water but also in saline

solutions. Thus, the AMPS monomer allows the synthesis of hydrogels with high water content, high mechanical stability and easy adaptability to the salinity of living organisms [42].

Hydrogels prepared using MBA crosslinker, AMPS and 2-dimethylaminoethyl methacrylate (DMAEMA) comonomers were also investigated to determine how the water absorption properties of the polymer networks change with changes in pH, temperature, saline concentration and solvent polarity. The water-containing networks exhibited temperature-sensitive behaviour with increasing weight percentage of AMPS. Furthermore, it has been demonstrated that this property can be easily varied by changing the composition [43].

In addition to the above, hydrogels of AMPS with various acrylamides have been studied. However, it has been confirmed that these two-component networks are mechanically not resistant and breaks easily. Yu and coworkers have demonstrated that sulfonate- Zr^{4+} metal coordination complexes can stabilize this structure. The resulting composite hydrogels contain moderate amounts of water, are less bendable, much stronger and harder to break. The extent of these properties depends on the amount of metal ions incorporated. In addition, the hydrogel retained the pH-sensitive behaviour of AMPS and it was demonstrated that the crosslink can be reconstituted back to its original metal complex-free form when treated with a basic solvent [44].

The first AMPS-PEG-based hydrogels were prepared by Karadağ and coworkers in 2009, where they prepared acrylamide-AMPS-PEG hydrogels for semi-IPN crosslinking with butanediol dimethacrylate (BDMA) and trimethylolpropane triacrylate (TMPTA) as crosslinkers [45].

Another article, also written in 2009, discusses the joint use of PEG and AMPS in a PEG-AMPS-PNIPAM mesh, in which the crosslinker was MBA. The synthesized network was investigated as a sodium diclofenac drug delivery system and demonstrated its near-complete and time-delayed drug delivery capability [46].

To the best of our knowledge, surprisingly there is no study in the literature in which a PEGDA-MPEGA-AMPS-containing hydrogel would have been prepared and systematically explored. During my research, taking into consideration of the unique and valuable properties of these compounds, and the expected properties of the resulting hydrogels, I have carried out series of systematic syntheses and characterization of the resulting conetwotks of AMPS-co-PEGA copolymers crosslinked with PEGDA.

3. OBJECTIVES

In the literature review, the importance of PEG-based hydrogels and hydrogels containing the AMPS monomer was described. It has been highlighted that the field of polymer networks containing novel types of ionic monomers is a very intensively investigated field nowadays. However, a thorough review of the literature did not reveal any study on the preparation of crosslinked polymers using a combination of PEG mono- and diacrylate and AMPS monomer, which is expected to provide unique characteristics for such hydrogels, especially in relation to their swelling behaviour and mechanical properties.

Therefore, the aim of my work is to prepare and characterize hydrogels using AMPS, MPEGA and PEGDA. My objective was to prepare such networks by free radical copolymerization by systematically varying the ratio of each reactant over a wide range of composition.

After the synthesis, my purpose was to characterize the success of the synthesis by determining the gel fraction value. Furthermore, I aimed to determine the equilibrium swelling degree of the produced networks in distilled water and different buffer solutions, and to study the optical properties of the hydrogels as well as their behaviour under mechanical stress. Thus, a comprehensive picture of the composition-property relationships can be obtained, which may allow the production of new types of hydrogels with predictable properties.

4. EXPERIMENTAL

4.1. Materials used

The materials used for the synthesis are summarised in **Table 1**.

Table 1: Materials and properties used for the production of hydrogels

Abbreviation	Material name	M (g/mol)	M_n	ρ (g/cm ³)	Mp (°C)	Bp (°C)
PEGDA	poly(ethylene glycol) diacrylate	-	700	1.120	17	224
MPEGA	methoxy poly(ethylene glycol) diacrylate	-	540	1.090	7	174
AMPS	2-acrylamino-2-methyl-1-propanesulfonic acid	207.24	-	1.100	195	-
V50	2,2'-Azobis(2-methylpropionamidine) dihydrochloride	271.19	-	0.42	175	267

The PEG derivatives used in my experiments contained inhibitors (100 ppm 4-methoxyphenol, 100, 300 ppm di-tert-butyl hydroxytoluene), which were removed immediately before use by permeation on a column filled with Al₂O₃. Other materials used in my experiments were applied directly without further purification.

4 2. Production of hydrogels

To prepare the hydrogels via free radical polymerization, a systematic series of experiments was performed in which the weight ratio of the PEGDA- MPEGA- AMPS components was varied. The polymerization was carried out at 60 °C with a reaction time of 12 hours. The amount of the reactants and distilled water as solvent used during the reactions are summarized in **Tables 2-11**.

Table 2: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-AMPS bicomponent conetworks

Name of experiment	Reagents			
	PEGDA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_AMPS_10_90	61.3	541.1	0.2	0.8
PEGDA_AMPS_20_80	119.3	479.7	0.2	0.8
PEGDA_AMPS_30_70	90.1	420.7	0.2	0.8
PEGDA_AMPS_40_60	237.6	358.0	0.2	0.8
PEGDA_AMPS_50_50	303.8	299.1	0.2	0.8
PEGDA_AMPS_60_40	358.9	239.4	0.2	0.8
PEGDA_AMPS_70_30	418.0	93.3	0.2	0.8
PEGDA_AMPS_80_20	481.5	118.4	0.2	0.8
PEGDA_AMPS_90_10	543.4	60.8	0.2	0.8
PEGDA_AMPS_100_0	597.7	-	0.2	0.8

Table 3: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 10 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_10_10_80	61.8	59.6	520.0	0.2	0.8
PEGDA_MPEGA_AMPS_10_30_60	58.0	176.1	363.9	0.2	0.8
PEGDA_MPEGA_AMPS_10_45_45	57.9	268.7	290.0	0.2	0.8
PEGDA_MPEGA_AMPS_10_60_30	60.9	358.0	178.9	0.2	0.8
PEGDA_MPEGA_AMPS_10_80_10	57.8	480.9	60.6	0.2	0.8

Table 4: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 20 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_20_10_70	117.0	57.6	419.1	0.2	0.8
PEGDA_MPEGA_AMPS_20_30_50	117.5	179.2	308.0	0.2	0.8
PEGDA_MPEGA_AMPS_20_40_40	122.4	236.5	238.3	0.2	0.8
PEGDA_MPEGA_AMPS_20_50_30	120.3	301.8	183.9	0.2	0.8
PEGDA_MPEGA_AMPS_20_70_10	122.6	419.6	59.3	0.2	0.8

Table 5: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 30 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_30_10_60	182.0	60.2	364.4	0.2	0.8
PEGDA_MPEGA_AMPS_30_20_50	181.9	117.2	297.4	0.2	0.8
PEGDA_MPEGA_AMPS_30_35_35	175.4	208.0	215.2	0.2	0.8
PEGDA_MPEGA_AMPS_30_50_20	177.4	296.9	120.7	0.2	0.8
PEGDA_MPEGA_AMPS_30_60_10	179.0	357.2	63.2	0.2	0.8

Table 6: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 40 % PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_40_10_50	242.5	61.0	313.5	0.2	0.8
PEGDA_MPEGA_AMPS_40_20_40	237.0	121.9	237.4	0.2	0.8
PEGDA_MPEGA_AMPS_40_30_30	237.1	179.2	182.1	0.2	0.8
PEGDA_MPEGA_AMPS_40_40_20	240.7	241.0	120.4	0.2	0.8
PEGDA_MPEGA_AMPS_40_50_10	242.4	298.7	57.9	0.2	0.8

Table 7: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 50 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_50_5_45	297.6	29.0	275.8	0.2	0.8
PEGDA_MPEGA_AMPS_50_15_35	303.8	89.5	208.4	0.2	0.8
PEGDA_MPEGA_AMPS_50_25_25	299.8	149.3	153.1	0.2	0.8
PEGDA_MPEGA_AMPS_50_35_15	300.8	211.7	92.0	0.2	0.8
PEGDA_MPEGA_AMPS_50_45_5	297.0	267.8	32.9	0.2	0.8

Table 8: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 60 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_60_10_30	365.0	57.1	177.0	0.2	0.8
PEGDA_MPEGA_AMPS_60_15_25	359.0	90.0	148.5	0.2	0.8
PEGDA_MPEGA_AMPS_60_20_20	361.2	117.1	129.0	0.2	0.8
PEGDA_MPEGA_AMPS_60_25_15	358.3	147.6	91.7	0.2	0.8
PEGDA_MPEGA_AMPS_60_30_10	357.6	178.2	61.7	0.2	0.8

Table 9: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 70 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_70_5_25	420.0	27.5	157.1	0.2	0.8
PEGDA_MPEGA_AMPS_70_10_20	367.6	85.2	144.6	0.2	0.8
PEGDA_MPEGA_AMPS_70_15_15	360.4	122.1	125.6	0.2	0.8
PEGDA_MPEGA_AMPS_70_20_10	360.8	153.0	97.1	0.2	0.8
PEGDA_MPEGA_AMPS_70_25_5	362.4	184.4	64.2	0.2	0.8

Table 10: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 80 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_80_4_16	482.1	23.3	95.6	0.2	0.8
PEGDA_MPEGA_AMPS_80_7_13	487.8	39.4	76.4	0.2	0.8
PEGDA_MPEGA_AMPS_80_10_10	475.6	56.0	58.4	0.2	0.8
PEGDA_MPEGA_AMPS_80_13_7	485.1	80.4	36.0	0.2	0.8
PEGDA_MPEGA_AMPS_80_16_4	484.2	91.6	24.4	0.2	0.8

Table 11: The amounts of the reactants and solvent (water) used in the preparation of PEGDA-MPEGA-AMPS conetworks with 90 wt% PEGDA content

Name of experiment	Reagents				
	PEGDA (mg)	MPEGA (mg)	AMPS (mg)	V50 stock solution (mL)	H ₂ O (mL)
PEGDA_MPEGA_AMPS_90_1_9	538.8	6.4	68.0	0.2	0.8
PEGDA_MPEGA_AMPS_90_3_7	535.2	17.6	38.8	0.2	0.8
PEGDA_MPEGA_AMPS_90_5_5	539.2	27.2	26.8	0.2	0.8
PEGDA_MPEGA_AMPS_90_7_3	539.4	38.0	17.4	0.2	0.8
PEGDA_MPEGA_AMPS_90_9_1	536.2	50.6	7.0	0.2	0.8

An aqueous stock solution of V50 initiator at a concentration of 3 mg/mL was measured into a vial, then the AMPS monomer at a concentration of 1 g/mL. The required amounts of the reactants indicated in **Table 2-11** were measured into a vial. The reaction mixture was homogenized and injected into septum-sealed 3 mL syringes, followed by bubbling N₂ gas through the reaction mixture for at least 10 min, deoxygenating it. Free radical polymerization was done by thermal initiation at 60 °C. The crosslinking was allowed to proceed for 12 hours. The produced hydrogels were then removed from the reaction chamber and extracted in pure ethanol for 3 days, changing the solvent every day. The ethanol extraction solvents were combined and then the networks were transferred into distilled water, which was changed daily for another 2 days.

4.3. Characterization of the produced hydrogels

4.3.1. Gel fraction

The success of the crosslinking was characterised by the gel fraction (*GF*), which indicates the percentage of the measured starting materials incorporated into the network. The gel fraction was determined using the following equation:

$$GF = \frac{m_d}{m_d + m_e}$$

where m_d is the mass of the dry hydrogel and m_e is the mass of the dry extract.

As I described earlier, the hydrogel purification was performed by extraction. The collected extracts were combined, evaporated using a rotary evaporator and

dried to a constant mass at 45 °C under vacuum. The cylindrical hydrogels, cleaned and swollen in water, were weighed and cut into 6 sections, weighed again and one section was dried at 45 °C under vacuum in an oven to a constant weight. The total dry mass of the sample was calculated by multiplying the mass of the swollen masses by the mass of the dried part.

4.3.2. Equilibrium degree of swelling

The equilibrium swelling degree (Q_e) describes the solvent uptake capacity of the networks. It indicates how many times the network can take up its own weight from a solvent. To calculate Q_e , I needed the mass of a hydrogel slice swollen in water and then dried. In Chapter 4.3.1, I measured the mass of each sample pieces when swollen to equilibrium in water and dried to mass stability. The equilibrium swelling degree was determined according to the following formula:

$$Q_e = \frac{m_s - m_d}{m_d}$$

where m_s is the mass of the swollen hydrogel slice and m_d is the mass of the dry hydrogel sample.

4.3.3. Determination of the pH-dependent swelling behaviour

Due to the presence of AMPS with a pK_a of 1.67 ± 0.5 , we can assume that the targeted conetworks will exhibit pH-sensitive characteristics. Determining the equilibrium degree of swelling in different buffer solutions provides essential information about the hydrogels' behavior under various pH-conditions from which we can, for example estimate their behavior in the human body. This behavior was tested in buffer solutions of pH = 2.00, pH = 5.00, pH = 7.00 and pH = 9.00. To determine the equilibrium swelling degree (Q_e) on each pH, the equation proposed in subchapter 4.3.2. was used.

4.3.4. Swelling measurements at different temperatures

In the literature summary, it's been introduced that MPEGA bears a thermally responsive behaviour, and it is expected to show up in the case of the hydrogels produced as well. This character was tested in conetworks containing 10 and 20 wt%

PEGDA, where the thermally sensitive behaviour of the crosslinker was negligible. The hydrogels were placed in distilled water, and then were heated from room temperature to 40 °C, and then gradually to 80 °C, while being weighed after every 10 °C of raise in temperature. The conetworks spent an hour on each temperature before being weighed. Afterwards, the equilibrium swelling degrees were determined to evaluate the reduced water uptake of the conetworks.

4.3.5. Mechanical measurements

Very valuable information about hydrogels can be obtained by studying their mechanical stability. The point of the measurement is to monitor the deformation of the meshes and their resistance to forces applied to them. For this reason, mechanical tests were also carried out on the prepared hydrogel samples using a TA.XT plus C Texture Analyzer stock measuring device. The measurements were made by measuring the size of the water-expanded samples with a precision digital caliper and then measuring the force required to deform the samples up to 25% deformation, covered with a teflon tape from the bottom up. I took the slope of the line fitted to the resulting data series $G - (\lambda - (1/\lambda^2))$ as the Young-modulus, where:

$G = F/A$ is the tension

F is the measured force (since this is given in units of mass, it is multiplied by 9.81 m/s²)

A is the area of the cross-section of the sample

$\lambda = l/l_0$ is the relative deformation

$l = l_0 - \Delta l$ is the current height

l_0 is the thickness of the sample

4.3.6. UV-Vis spectroscopy measurements

We can also obtain valuable information by studying the optical properties of hydrogels. By knowing the optical properties, it is possible to determine whether a particular hydrogel can be used for the production of different optical sensors, as a contact lens material, or in other applications requiring high transmittance.

The hydrogel samples I prepared were translucent, and in order to quantify this accurately, I used UV-Vis spectroscopy to investigate the absorbance and transmittance of each hydrogel as a function of wavelength. The measurements were carried out with a Jasco V-650 spectrophotometer. The samples, swollen in

water, were placed in a standard 1×1 cm quartz cuvette filled with distilled water using a suitable fixture. Measurements were performed in the 200-800 nm range at 25 °C using distilled water as a reference.

5. RESULTS AND DISCUSSION

In my work, I prepared and tested crosslinked polymers containing both 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) ionic monomer and mono- and bi-acrylate functional PEG, and systematically varied their ratios.

After preparation, my work aimed to characterize the success of the synthesis by determining the gel fraction. Afterwards, my objective was to determine the equilibrium swelling degree values of the synthesized hydrogels in distilled water, different buffer solutions and then in distilled water, under various temperatures. Lastly, I focused on investigating the behaviour of the networks under mechanical stress and studied the optical properties of the hydrogels in the whole UV and visible light range. This research will allow a comprehensive and detailed view on the composition-property relationships of the samples to be obtained. By examining the measured parameters as a function of composition, production of hydrogels with predictable properties may be possible.

The success of hydrogel production was characterized by the gel fraction (*GF*) values shown in **Table 12**. As can be seen, in all cases the *GF* values are above 75%, which means that, the rate of the incorporation of comonomers into the polymer network is sufficiently high. These results suggest that the polymer networks are containing the reactants in close proportion to the preparation measurements.

Table 12: The networks' gel fraction (*GF*) and equilibrium swelling degree (Q_e) in water and various buffer solutions

Names	$Q_e\%$					<i>GF</i> %
	Distilled water	pH=9.00	pH=7.00	pH=5.00	pH=2.00	
PEGDA_AMPS_10_90	2207	1288	1290	1345	1412	78
PEGDA_AMPS_20_80	1463	871	887	893	944	86
PEGDA_AMPS_30_70	701	580	816	881	890	85
PEGDA_AMPS_40_60	591	524	546	585	609	92
PEGDA_AMPS_50_50	437	415	430	449	498	85
PEGDA_AMPS_60_40	407	359	388	447	487	76
PEGDA_AMPS_70_30	355	318	329	342	370	78
PEGDA_AMPS_80_20	342	220	301	342	359	77
PEGDA_AMPS_90_10	278	211	296	299	311	79

Names	Q _e %					GF%
	Distilled water	pH=9.00	pH=7.00	pH=5.00	pH=2.00	
PEGDA_MPEGA_AMPS_10_10_80	2589	1871	2331	2774	3849	77
PEGDA_MPEGA_AMPS_10_30_60	1332	940	1111	1122	1177	78
PEGDA_MPEGA_AMPS_10_45_45	1012	828	840	877	921	85
PEGDA_MPEGA_AMPS_10_60_30	853	623	706	720	907	90
PEGDA_MPEGA_AMPS_10_80_10	653	525	578	590	717	78
PEGDA_MPEGA_AMPS_20_10_70	2086	1523	1586	1768	3212	88
PEGDA_MPEGA_AMPS_20_30_50	1038	1268	1297	1529	1785	82
PEGDA_MPEGA_AMPS_20_40_40	713	542	555	597	748	77
PEGDA_MPEGA_AMPS_20_50_30	704	488	508	560	738	80
PEGDA_MPEGA_AMPS_20_70_10	665	481	499	529	647	78
PEGDA_MPEGA_AMPS_30_10_60	913	836	836	826	938	83
PEGDA_MPEGA_AMPS_30_20_50	887	758	790	852	858	88
PEGDA_MPEGA_AMPS_30_35_35	588	631	639	644	731	77
PEGDA_MPEGA_AMPS_30_50_20	615	490	521	570	695	80
PEGDA_MPEGA_AMPS_30_60_10	473	394	415	443	615	83
PEGDA_MPEGA_AMPS_40_10_50	578	505	519	560	674	82
PEGDA_MPEGA_AMPS_40_20_40	554	500	510	531	552	92
PEGDA_MPEGA_AMPS_40_30_30	504	461	493	487	540	86
PEGDA_MPEGA_AMPS_40_40_20	481	477	480	495	526	86
PEGDA_MPEGA_AMPS_40_50_10	449	345	370	401	503	79
PEGDA_MPEGA_AMPS_50_5_45	502	438	594	601	670	81
PEGDA_MPEGA_AMPS_50_15_35	464	422	564	594	632	82
PEGDA_MPEGA_AMPS_50_25_25	443	363	476	483	529	91
PEGDA_MPEGA_AMPS_50_35_15	426	300	386	320	456	84
PEGDA_MPEGA_AMPS_50_45_5	363	271	307	409	437	86
PEGDA_MPEGA_AMPS_60_10_30	447	297	309	340	432	93
PEGDA_MPEGA_AMPS_60_15_25	432	293	301	327	413	85
PEGDA_MPEGA_AMPS_60_20_20	359	285	296	315	411	96
PEGDA_MPEGA_AMPS_60_25_15	330	268	276	311	410	81
PEGDA_MPEGA_AMPS_60_30_10	323	248	265	306	409	89
PEGDA_MPEGA_AMPS_70_5_25	358	255	308	324	364	81
PEGDA_MPEGA_AMPS_70_10_20	350	251	301	320	350	90
PEGDA_MPEGA_AMPS_70_15_15	330	240	289	317	345	96
PEGDA_MPEGA_AMPS_70_20_10	326	237	270	306	332	90
PEGDA_MPEGA_AMPS_70_25_5	320	220	584	283	303	91

Names	$Q_e\%$					$GF\%$
	Distilled water	pH=9.00	pH=7.00	pH=5.00	pH=2.00	
PEGDA_MPEGA_AMPS_80_4_16	369	239	302	310	374	81
PEGDA_MPEGA_AMPS_80_7_13	360	213	256	274	351	85
PEGDA_MPEGA_AMPS_80_10_10	315	202	248	254	322	79
PEGDA_MPEGA_AMPS_80_13_7	337	199	210	220	319	83
PEGDA_MPEGA_AMPS_80_16_4	333	183	196	203	311	79
PEGDA_MPEGA_AMPS_90_1_9	302	199	209	284	332	85
PEGDA_MPEGA_AMPS_90_3_7	291	183	193	227	326	81
PEGDA_MPEGA_AMPS_90_5_5	286	180	190	219	288	87
PEGDA_MPEGA_AMPS_90_7_3	270	175	186	204	277	80
PEGDA_MPEGA_AMPS_90_9_1	267	159	172	195	213	86

Studying the swelling properties of the hydrogels was one of the most important parts of my work. With the incorporation of AMPS, a monomer containing an ionic sulfate group and protonated amide group, the extent of which depends on pH we can expect that the water absorption and water retention capacity of the networks will be significantly increased. In addition, the MPEGA comonomer also exhibits hydrophilic characteristics, but due to its larger size, it is expected to have a significant effect on the equilibrium swelling degree values. The determined equilibrium swelling degrees (Q_e) of all produced hydrogel are also presented in **Table 12**.

As mentioned above, I have plotted the equilibrium swelling degree values of a series of hydrogel experiments as a function of their AMPS content. As shown in **Figure 6**, the Q_e values of the two-component series, i.e. the PEGA-AMPS conetworks, range from 200% to 2200%, and as expected, increasing swelling is observed with increasing AMPS content. On the basis of this finding, it can be concluded that the PEGDA-AMPS conetworks with higher than 80 wt% AMPS content behave as superabsorbent hydrogels.

In all cases of the three-component conetworks, it is observed that the Q_e values of the respective series show a strictly monotonic increase with increasing AMPS content. It can be also stated that by increasing the PEGDA crosslinker ratio, the Q_e values decreases, which in part is due to the increase of the crosslinking density, i.e. to the decrease in the N_c (the average number of monomer units

between two crosslinking points), and simultaneously also to the decrease of the relative amounts of the hydrophilic PEGA and AMPS in these conetworks.

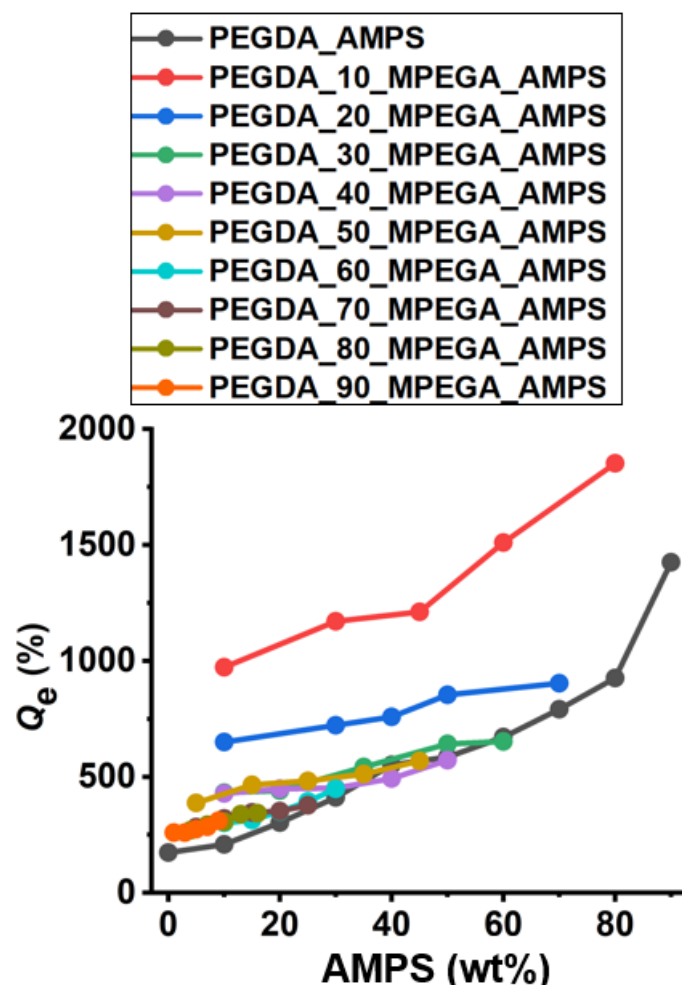


Figure 6: *Plot of equilibrium swelling degrees of PEGDA-MPEGA-AMPS hydrogels as a function of AMPS content*

Figure 6 also clearly shows that the incorporation of the MPEGA comonomer in the network can further increase the water absorption capacity. The difference is most striking for the series with 10% and 20% PEGDA content. The PEGDA_AMPS_10_90 networks show an equilibrium swelling of 1400%, while the Q_e of the two-component network with 20% PEGDA is 800%. In comparison, the PEGDA_MPEGA_AMPS_10_10_80 networks with 10% less AMPS content show a very significant equilibrium swelling of approximately 1000%. Furthermore, it is observed that, although the Q_e values of the three-component conetworks move towards the Q_e values of the two-component conetworks with increasing PEGDA content, they remain above them in every instance. This suggests that the presence of even a few percent of AMPS has a significant influence on the water absorption capacity of these hydrogels. In addition, I would point out that the complete three-

component series containing 10% PEGDA and the 10% PEGDA-AMPS two-component hydrogels show Q_e values above 1000%, which means that these hydrogels, which have not been investigated before, behave as superabsorbents.

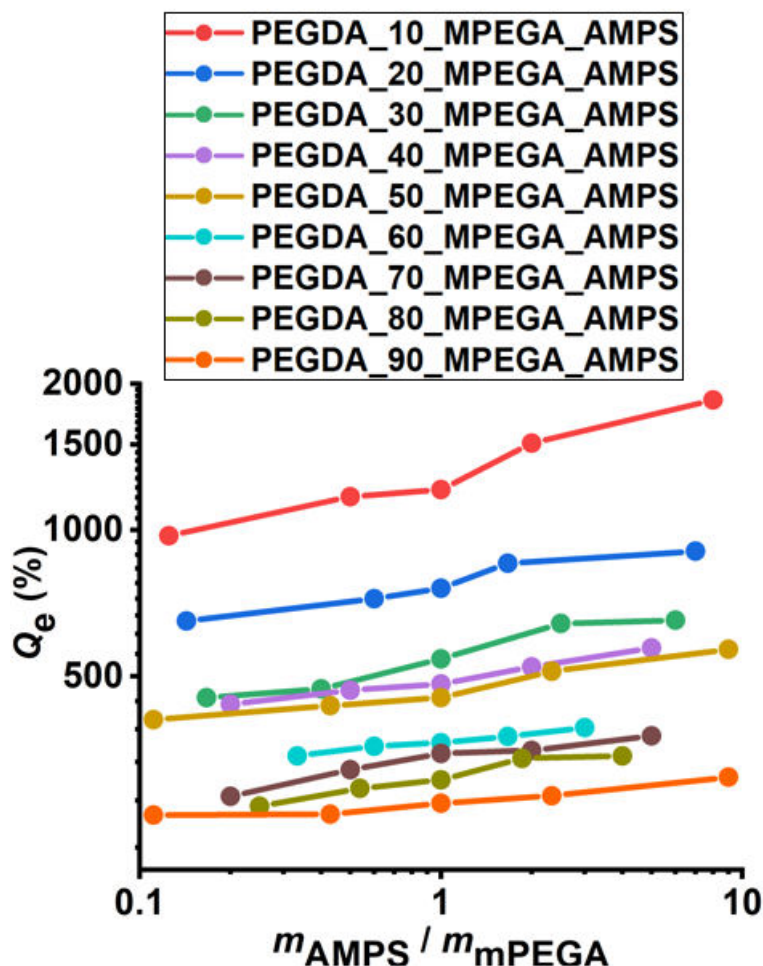


Figure 7: Equilibrium swelling degree values of different PEGDA conetwork series as a function of m_{AMPS}/m_{MPEGA} ratio

For a better overview of the effect of the composition on the swelling property in each three-component series, the Q_e of each PEGDA crosslinked series are plotted as a function of the mass fraction of the comonomers, i.e. AMPS and MPEGA, in **Figure 7**. In this way, it is easy to see and interpret the effect of the amount of the two comonomers within each series, regardless of their combined maximum amount. It can be clearly seen, that increasing the PEGDA crosslinker content results in a decrease in the equilibrium swelling degree, while increasing the AMPS content results in an increase in the Q_e values. The data in Figure 7 also indicate that while for low PEGDA content the Q_e increases steeply, with

increasing AMPS/MPEGA ratio, i.e., with increasing the amount of AMPS, this effect is significantly smaller.

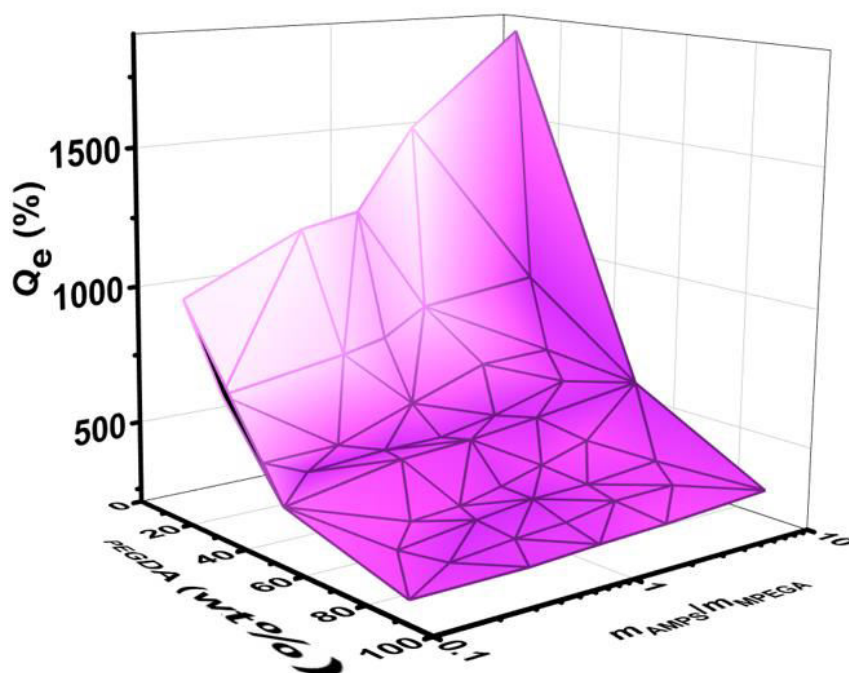


Figure 8: Three-dimensional representation of Q_e values

I have also plotted the results on a three-dimensional graph, shown in **Figure 8**. In this three-dimensional plot, I plotted the equilibrium swelling degree values of the hydrogels as the function of the PEGDA crosslinker content (x -axis) and as the AMPS/MPEGA comonomer mass ratios (y axis). Using the resulting surface, it can be easily assigned crosslinker and comonomer mass ratios to arbitrarily chosen equilibrium swelling degrees, allowing the production of hydrogels with AMPS content and predictable and predetermined properties.

As can be seen in **Table 12** and **Figures 9-18**, the swelling degrees measured in the different buffer solutions increase with decreasing pH, reaching only half of the values measured in distilled water and at pH = 9 and exceeding them in several cases at pH = 2. The Q_e values increase in proportion to the AMPS content at each pH as well, due to AMPS's ionic nature. The values measured in distilled water, however, do not fit into the series of swelling degrees measured in the buffer solutions, because the conetworks swollen in water are not affected by the ionic strengths of the buffer solutions. Thus, the Q_e values of the hydrogels swollen in distilled water usually fall between the values measured at pH=2 and pH=5. Based on these results, it is possible to design a 3-component hydrogel with the desired degree of swelling not only in distilled water but also at a given pH.

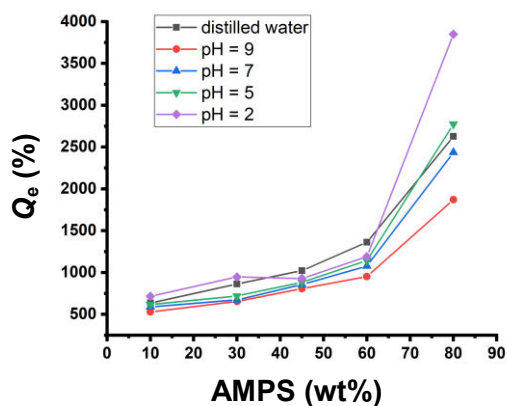


Figure 9: Equilibrium swelling degrees at different pH of 10 Wt% PEGDA-containing networks

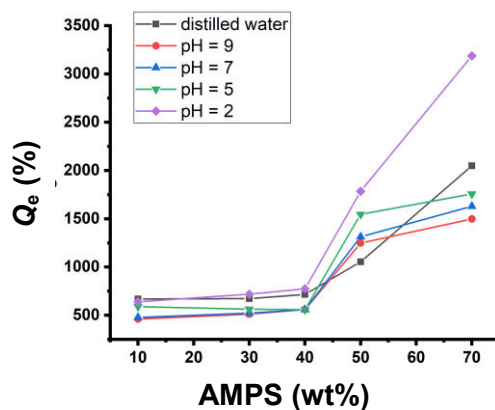


Figure 10: Equilibrium swelling degrees at different pH of 20 Wt% PEGDA-containing networks

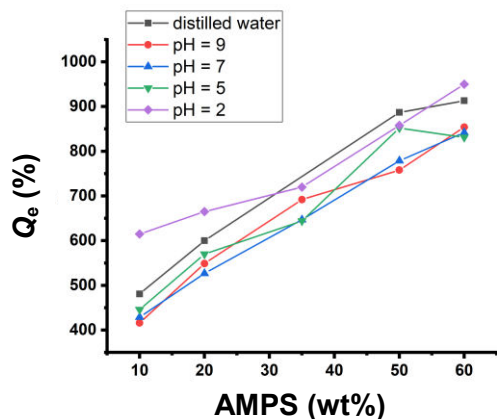


Figure 11: Equilibrium swelling degrees at different pH of 30 Wt% PEGDA-containing networks

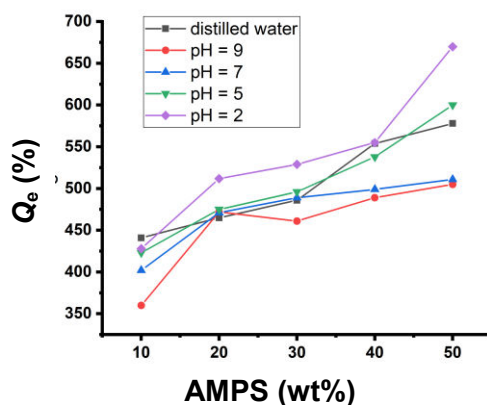


Figure 12: Equilibrium swelling degrees at different pH of 40 Wt% PEGDA-containing networks

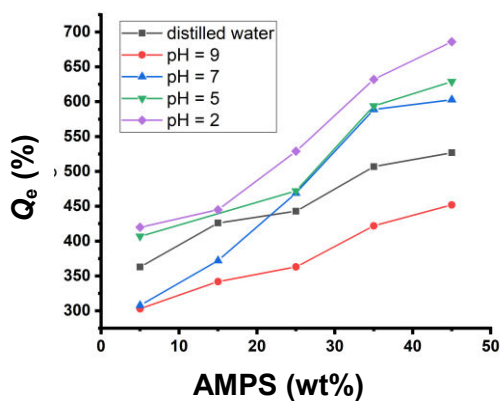


Figure 13: Equilibrium swelling degrees at different pH of 50 Wt% PEGDA-containing networks

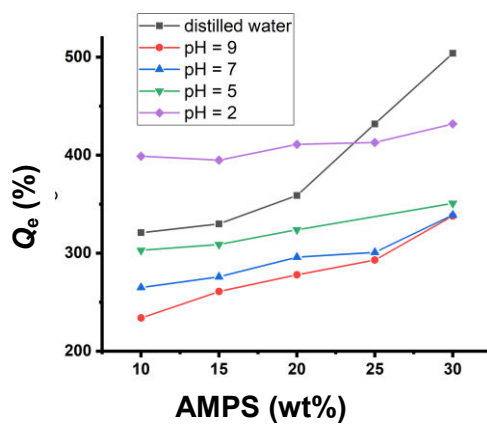


Figure 14: Equilibrium swelling degrees at different pH of 60 Wt% PEGDA-containing networks

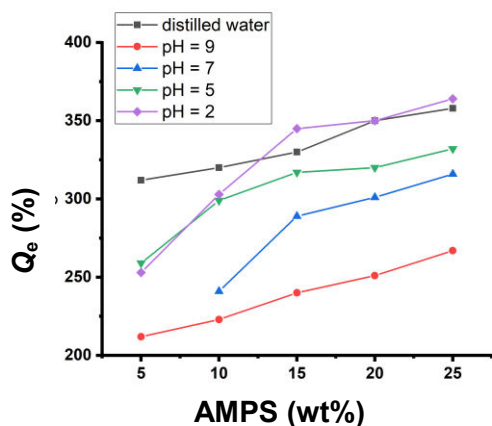


Figure 15: Equilibrium swelling degrees at different pH of 70 Wt% PEGDA-containing networks

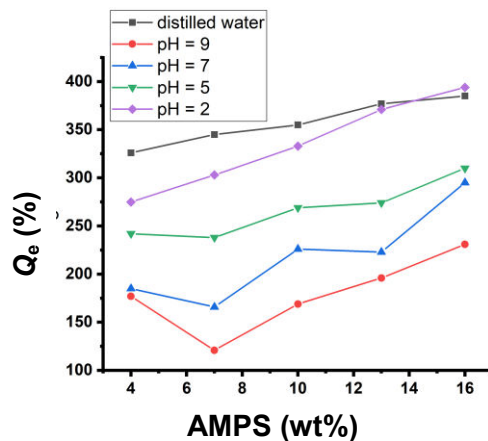


Figure 16: Equilibrium swelling degrees at different pH of 80 Wt% PEGDA-containing networks

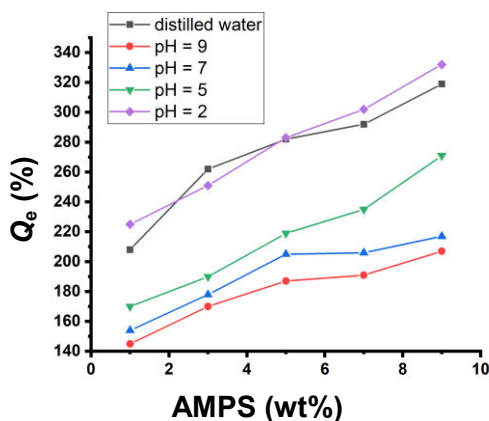


Figure 17: Equilibrium swelling degrees at different pH of 90 Wt% PEGDA-containing networks

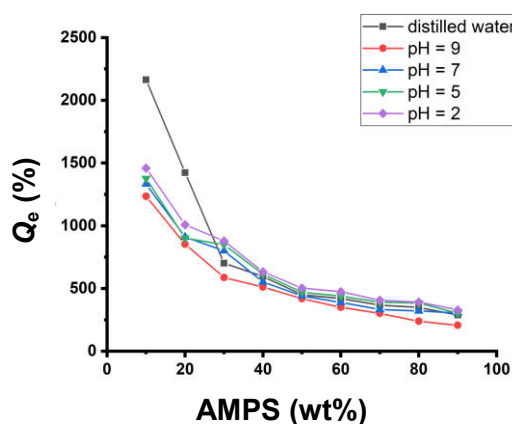
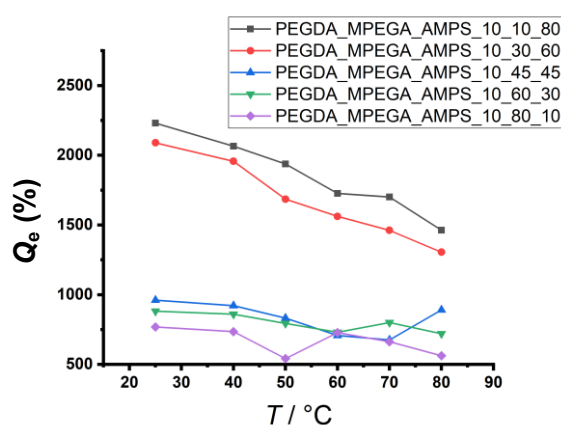
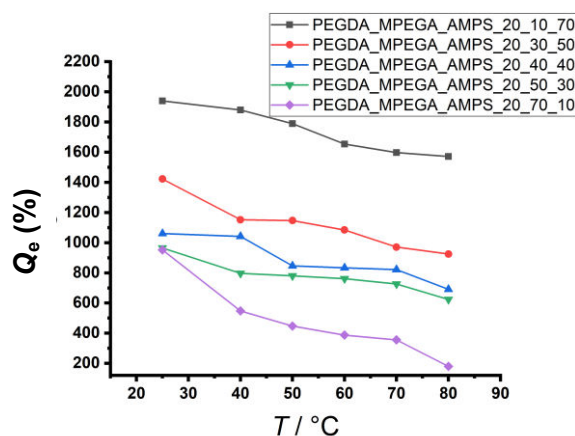


Figure 18: Equilibrium swelling degrees at different pH of the two-component conetworks

As shown in **Table 13** and **Figures 19-20**, monotonous decrease of the swelling degrees with increasing temperature is observed for the hydrogels containing 10 and 20 wt% PEGDA. This is mainly due to the effect of the dependence of hydration of the polymer chains as a function of the temperature. Increasing the temperature from room temperature to 80 °C, the most significant change in the swelling degree, nearly one order of magnitude takes place in the case of the PEGDA_MPEGA_APMS 20_70_10 sample. The rest of the investigated samples show slighter temperature sensitivity in terms of their swelling behaviour.

Table 13: Equilibrium swelling degrees in distilled water at different temperatures

Names	25 °C Q _e %	40 °C Q _e %	50 °C Q _e %	60 °C Q _e %	70 °C Q _e %	80 °C Q _e %
PEGDA_MPEGA_AMPS_10_10_80	2231	2065	1938	1726	1701	1463
PEGDA_MPEGA_AMPS_10_30_60	2090	1957	1686	1562	1462	1305
PEGDA_MPEGA_AMPS_10_45_45	961	922	832	707	676	891
PEGDA_MPEGA_AMPS_10_60_30	882	860	795	731	800	721
PEGDA_MPEGA_AMPS_10_80_10	769	736	543	728	663	562
PEGDA_MPEGA_AMPS_20_10_70	1940	1880	1790	1654	1598	1572
PEGDA_MPEGA_AMPS_20_30_50	1423	1152	1147	1085	971	925
PEGDA_MPEGA_AMPS_20_40_40	1061	1042	846	833	822	691
PEGDA_MPEGA_AMPS_20_50_30	966	797	781	762	727	624
PEGDA_MPEGA_AMPS_20_70_10	952	548	448	388	356	181

**Figure 19:** Equilibrium swelling degrees of 10 Wt% PEGDA hydrogels in distilled water, on different temperatures**Figure 20:** Equilibrium swelling degrees of 20 Wt% PEGDA hydrogels in distilled water, on different temperatures

The slight thermal sensitivity is illustrated visually by one of the MPEGAs-rich hydrogels, PEGDA_MPEGA_AMPS_10_60_30, in **Figures 21-23**. These photos, taken on the same swollen sample at 25 °C, 70 °C and 80 °C, clearly show the slight decrease in the diameter of the hydrogel with increasing temperature in accordance with the change of the swelling degree from 880% to 800% and 720%, respectively. This observation indicate that the PEGDA_MPEGA_AMPS hydrogels are stable materials in a broad temperature range, and in most cases only modest changes occur in the swelling degrees. It can be concluded that these findings might be important for applications of these conetworks within the examined temperature range. .

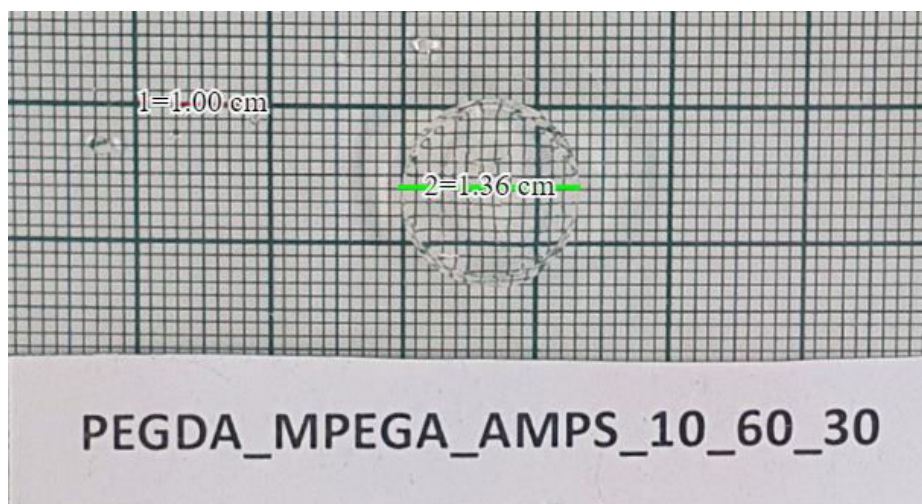


Figure 21: Diamater of PEGDA_MPEGA_AMPS_10_60_30 at 25 °C

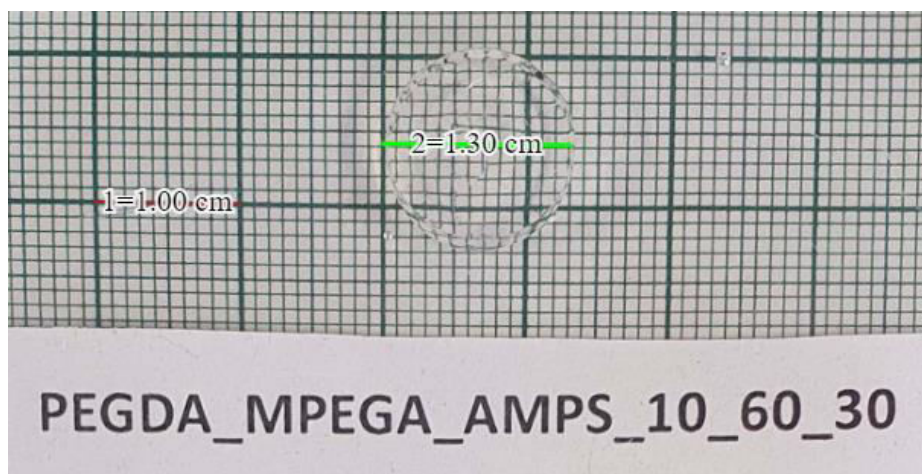


Figure 22: Diamater of PEGDA_MPEGA_AMPS_10_60_30 at 70 °C

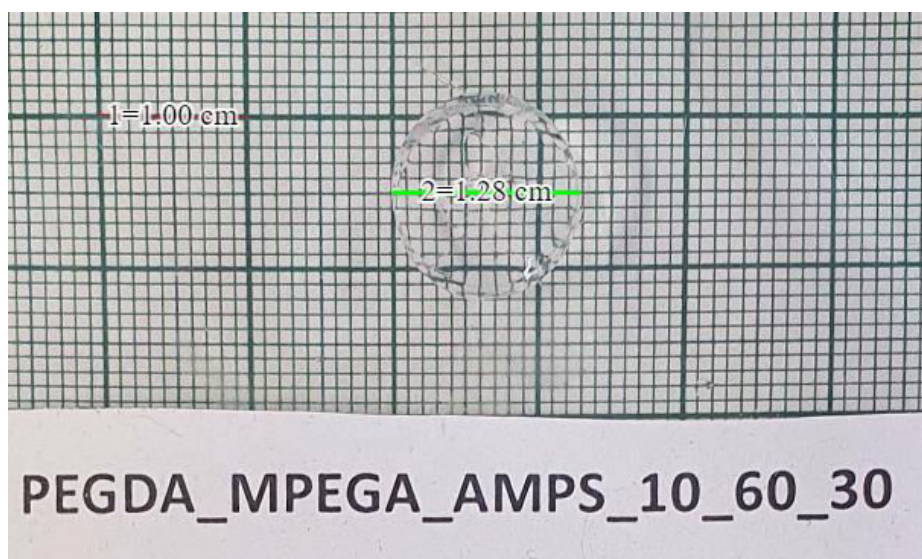


Figure 23: Diamater of PEGDA_MPEGA_AMPS_10_60_30 at 80 °C

Another important property of hydrogels, which has a significant impact on their use is their mechanical stability. For this reason, Stress-strain measurements were carried out with PEGDA_MPEGA_AMPS hydrogels. For the evaluation of these measurements, the stress is plotted as a function of relative deformation, and the slopes of the lines fitted to this function corresponds to the Young's moduli of the samples. The mechanical curve of one representative sample (PEGDA_AMPS_10_90 hydrogel) is shown in **Figure 24**. The mechanical curves of the other samples are shown in **Figures F.1-F.54** in the Appendix.

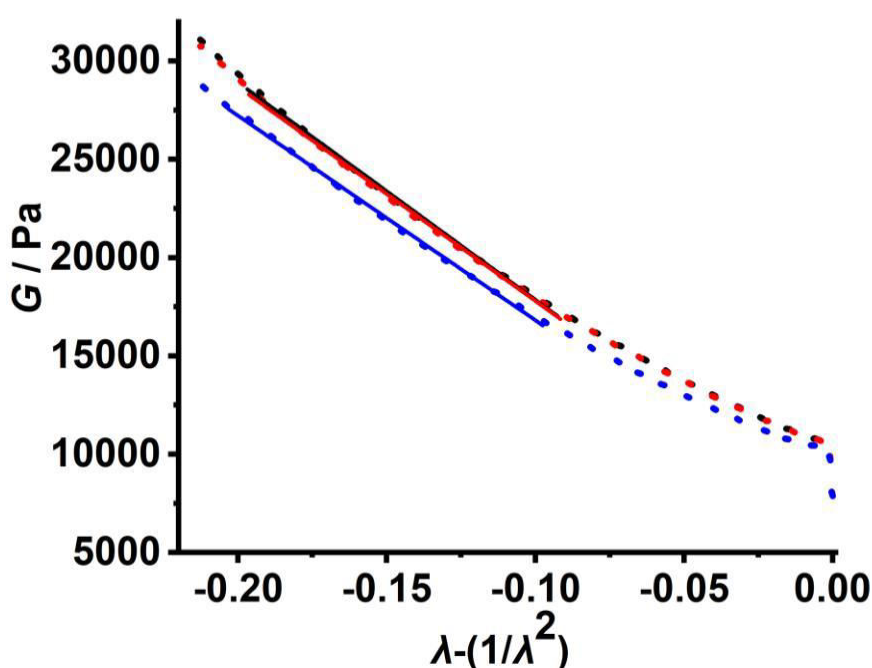


Figure 24: *The stress-strain curve of PEGDA_AMPS_10_90 hydrogel*

The Young's modulus values of the complete series of hydrogels are shown in **Table 14**, and the results are displayed graphically in **Figures 25** and **26**. The Young's modulus plots of some hydrogel series are shown in **Figures F.55-F.64** in the Appendix.

Table 14: Young's modulus values of PEGDA-AMPS and PEGDA-MPEGA-AMPS hydrogels

Name of the experiment	<i>Young modulus (N/m²)</i>
PEGDA_AMPS_10_90	31290
PEGDA_AMPS_20_80	31420
PEGDA_AMPS_30_70	28370
PEGDA_AMPS_40_60	54870
PEGDA_AMPS_50_50	58020
PEGDA_AMPS_60_40	67120
PEGDA_AMPS_70_30	76140
PEGDA_AMPS_80_20	107770
PEGDA_AMPS_90_10	116450
PEGDA_AMPS_100_0	138620
PEGDA_MPEGA_AMPS_10_10_80	10700
PEGDA_MPEGA_AMPS_10_30_60	16670
PEGDA_MPEGA_AMPS_10_45_45	25550
PEGDA_MPEGA_AMPS_10_60_30	51230
PEGDA_MPEGA_AMPS_10_80_10	70890
PEGDA_MPEGA_AMPS_20_10_70	10340
PEGDA_MPEGA_AMPS_20_30_50	18030
PEGDA_MPEGA_AMPS_20_40_40	19130
PEGDA_MPEGA_AMPS_20_50_30	73650
PEGDA_MPEGA_AMPS_20_70_10	43530
PEGDA_MPEGA_AMPS_30_10_60	12990
PEGDA_MPEGA_AMPS_30_20_50	49190
PEGDA_MPEGA_AMPS_30_35_35	59240
PEGDA_MPEGA_AMPS_30_50_20	75110
PEGDA_MPEGA_AMPS_30_60_10	75020
PEGDA_MPEGA_AMPS_40_10_50	28320
PEGDA_MPEGA_AMPS_40_20_40	46890
PEGDA_MPEGA_AMPS_40_30_30	67190
PEGDA_MPEGA_AMPS_40_40_20	65780
PEGDA_MPEGA_AMPS_40_50_10	86850
PEGDA_MPEGA_AMPS_50_5_45	28050
PEGDA_MPEGA_AMPS_50_15_35	36890
PEGDA_MPEGA_AMPS_50_25_25	56260
PEGDA_MPEGA_AMPS_50_35_15	97890
PEGDA_MPEGA_AMPS_50_45_5	108290

Name of the experiment	<i>Young modulus (N/m²)</i>
PEGDA_MPEGA_AMPS_60_10_30	47850
PEGDA_MPEGA_AMPS_60_15_25	83030
PEGDA_MPEGA_AMPS_60_20_20	184520
PEGDA_MPEGA_AMPS_60_25_15	103370
PEGDA_MPEGA_AMPS_60_30_10	115430
PEGDA_MPEGA_AMPS_70_5_25	11510
PEGDA_MPEGA_AMPS_70_10_20	34470
PEGDA_MPEGA_AMPS_70_15_15	32700
PEGDA_MPEGA_AMPS_70_20_10	82060
PEGDA_MPEGA_AMPS_70_25_5	140380
PEGDA_MPEGA_AMPS_80_4_16	57210
PEGDA_MPEGA_AMPS_80_7_13	63610
PEGDA_MPEGA_AMPS_80_10_10	66320
PEGDA_MPEGA_AMPS_80_13_7	166510
PEGDA_MPEGA_AMPS_80_16_4	193620
PEGDA_MPEGA_AMPS_90_1_9	74600
PEGDA_MPEGA_AMPS_90_3_7	293400
PEGDA_MPEGA_AMPS_90_5_5	335690
PEGDA_MPEGA_AMPS_90_7_3	370610
PEGDA_MPEGA_AMPS_90_9_1	374350

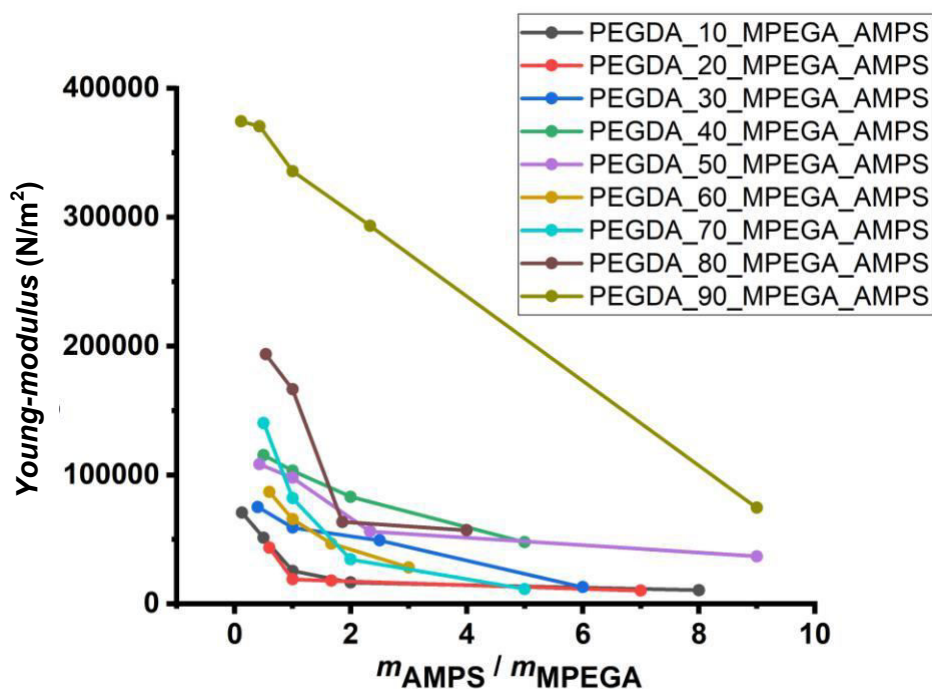


Figure 25: Young modulus values of PEGDA-AMPS and PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS content

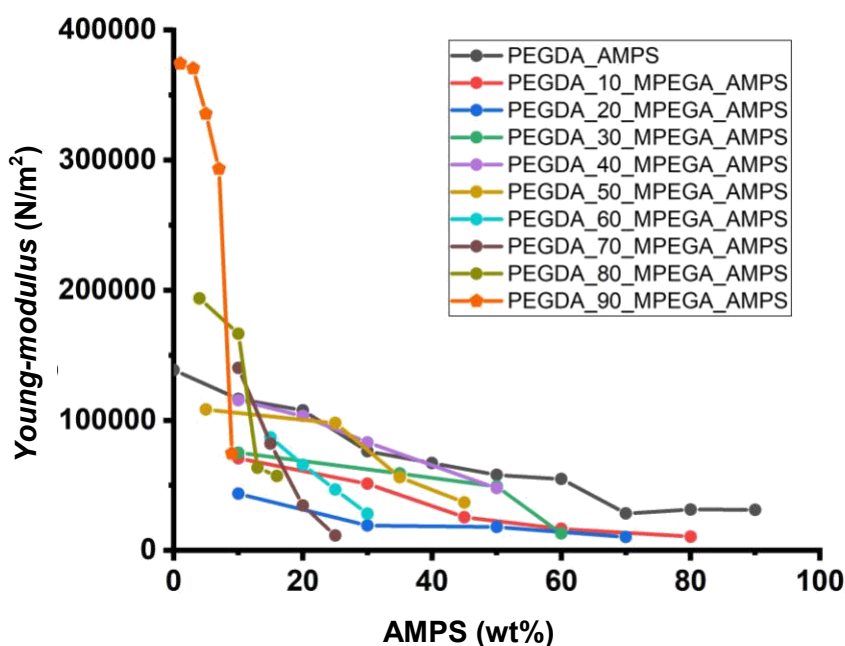


Figure 26: Young- modulus values of different PEGDA crosslinker-containing crosslinker series as a function of the ratio of AMPS and MPEGA comonomers

Based on the results of **Table 14** and **Figures 25** and **26**, it can be concluded that, as expected, increasing the PEGDA crosslinker content increases the hydrogels' mechanical stability. In other words, the higher the crosslinker content of the samples, the harder and more resistant a network is. This is due to the fact that in

the case of hydrogels with high AMPS contents, the high water content makes the networks softer, easier to bend, but more fragile. In most cases, a significant decrease in the modulus is observed until a ratio of AMPS:MPEGA of 2:1 is reached, and above this ratio much smaller decrease in the Young's modulus is obtained.

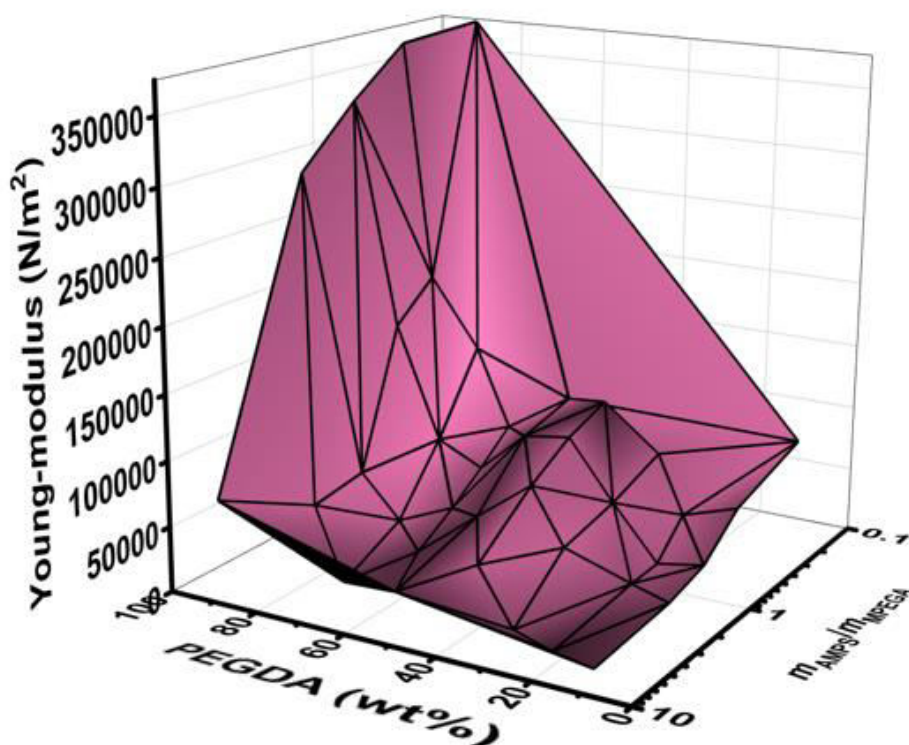


Figure 27: *Young's modulus values of different PEGDA crosslinker crosslinker series as a function of the ratio of comonomers and PEGDA content*

As for the equilibrium swelling degrees, a three-dimensional representation of PEGDA content, AMPS/MPEGA comonomer ratio, Young's modulus can be constructed from Young's modulus values as shown in **Figure 27**. This Figure clearly shows both the increase in Young's modulus value with increasing PEGDA ratio and the increase in Young's modulus value with decreasing AMPS and MPEGA mass ratio. The Young's modulus values produce a surface, which, although not an accurate approximation, is a good estimate for determining the mechanical stability of a crosslinked composition.

Taking into account the importance of the optical properties of hydrogels, the absorbance and transmittance of the investigated swollen conetworks as a function of wavelength was determined by by a UV-Vis spectrophotometer. The measured absorbance and transmittance values of a representative sample, the PEGDA_AMPS two-component crosslinked series, as a function of wavelength are shown in **Figures**

28 and **29**. The results of the other series are shown in **Figures F.65-F.82** in the Appendix.

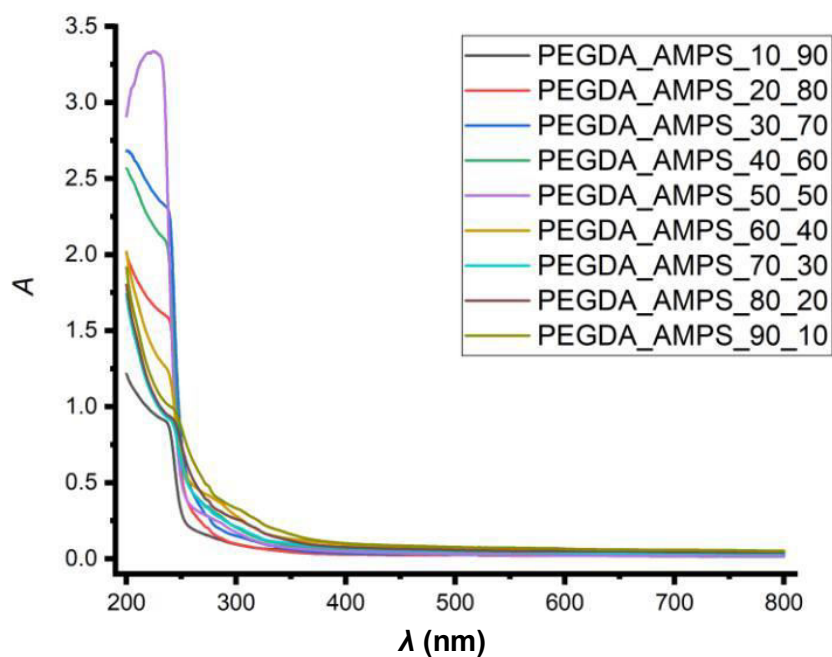


Figure 28: Absorbance of PEGDA_AMPS hydrogel samples with different compositions as a function of wavelength

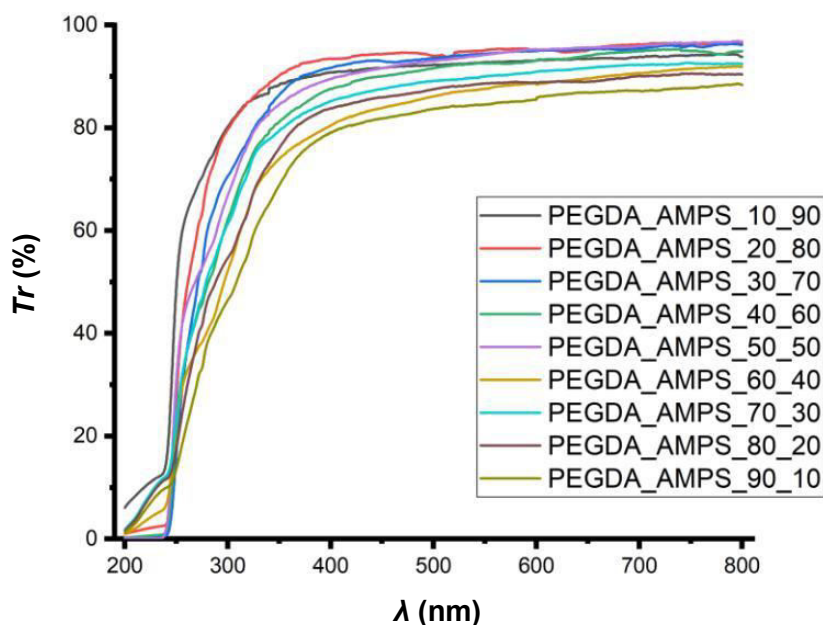


Figure 29: Transmittance of PEGDA_AMPS hydrogel samples with different compositions as a function of wavelength

Both the absorbance and transmittance curves clearly indicate that the swollen hydrogels investigated have negligible absorption in the visible light region, i.e. the measured absorbance is below 0.25. In contrast, the absorbance sharply increases above 1 in the UV region. This opacity allows the use of the PEGDA-PEGA-AMPS conetworks for various optical applications.

6.SUMMARY

Polymers containing ionic monomers have gained significant attention in recent years. In my work, a unique series of polymer conetworks composed of the biocompatible poly(ethylene glycol) diacrylate (PEGDA), methoxy poly(ethylene glycol) acrylate (MPEGA) and the zwitterionic 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were successfully synthesized by free radical copolymerization in a broad range of systematically varied composition. In these conetworks, the PEGDA chains are the macromolecular crosslinkers of the MPEGA-co-AMPS copolymers. Because detailed studies cannot be found about such conetworks and their hydrogels, my studies were expected to provide valuable new information on the characteristics of PEG-based hydrogels containing AMPS as an ionic monomer.

The systematic polymerization experiments resulted in stable gels with high gel fractions, which possess strong composition dependent equilibrium swelling degrees in water, ranging from low swelling capacities to even superabsorbent properties. The evaluation of the equilibrium swelling degrees as a function of the conetworks' composition led to a previously unknown correlation between these parameters, which indicate that the swelling characteristics can be precisely controlled by composition in a very broad range.

Due to the ionic AMPS content, these hydrogels perform pH-sensitive swelling behavior, that is, increased equilibrium swelling degrees at low pH, which decreases with increasing pH values. This is attributed to the extent of the protonation of the amide groups in the AMPS comonomer.

The investigated conetworks show thermally sensitive swelling properties, that is decreasing swelling degrees with increasing temperature. The extent of swelling of the MPEGA-rich conetworks is especially sensitive to the temperature, as nearly one order of magnitude decline is observed by increasing the temperature up to 80 °C.

The mechanical measurements indicate significant structural influence on the Young moduli of the investigated hydrogels, which are in the range of 10^3 - $370 \cdot 10^3$ N/m². It was found that increasing the AMPS content considerably decreases the mechanical robustness, making the gels soft and easy to bend.

The UV-Vis spectroscopic measurements of the swollen conetwork hydrogels show that these are completely transparent in the visible light region, offering potential photonic application options. In contrast, due to the presence of the UV

absorbing carbonyl groups, they show significant absorption in the UV range, thus providing UV-protection possibilities.

Based on the obtained results, especially on the found composition-property relationships, it can be stated that hydrogels of the new conetworks of AMPS-*co*-PEG copolymers crosslinked by PEGDA can be produced with predetermined equilibrium swelling degrees, as well as estimated mechanical stability and good optical transparency.

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9. APPENDIX

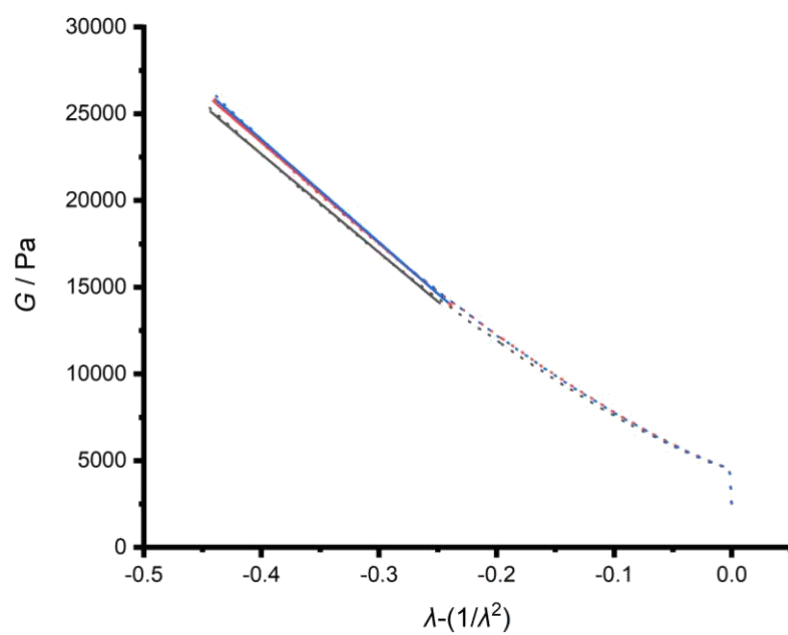


Figure F.1: The stress-strain curve of PEGDA_AMPS_20_80 hydrogel

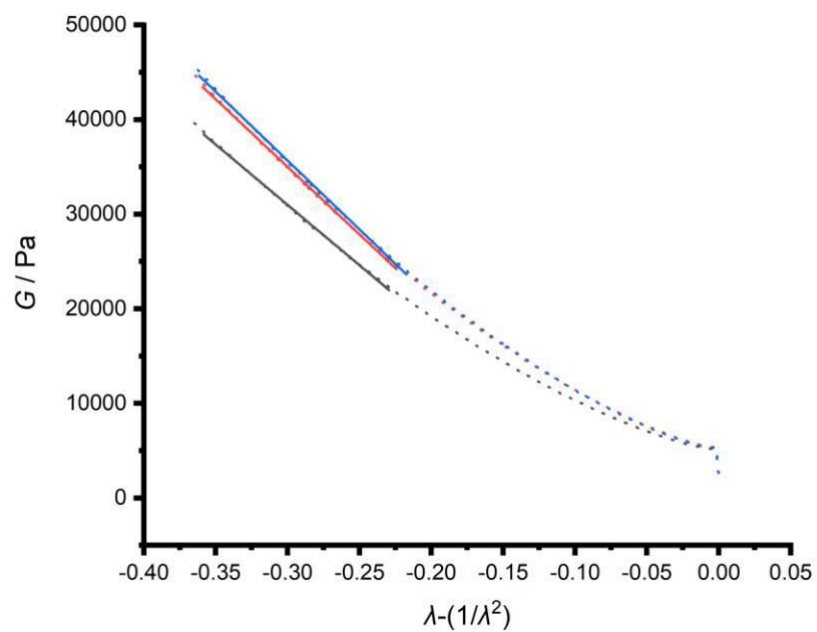


Figure F.2: The stress-strain curve of PEGDA_AMPS_30_70 hydrogel

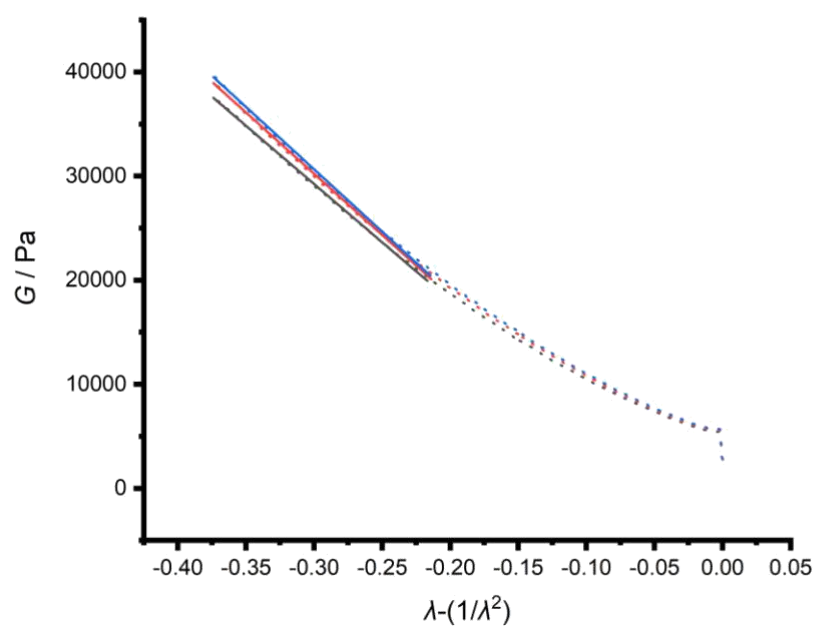


Figure F.3: The stress-strain curve of PEGDA_AMPS_40_60 hydrogel

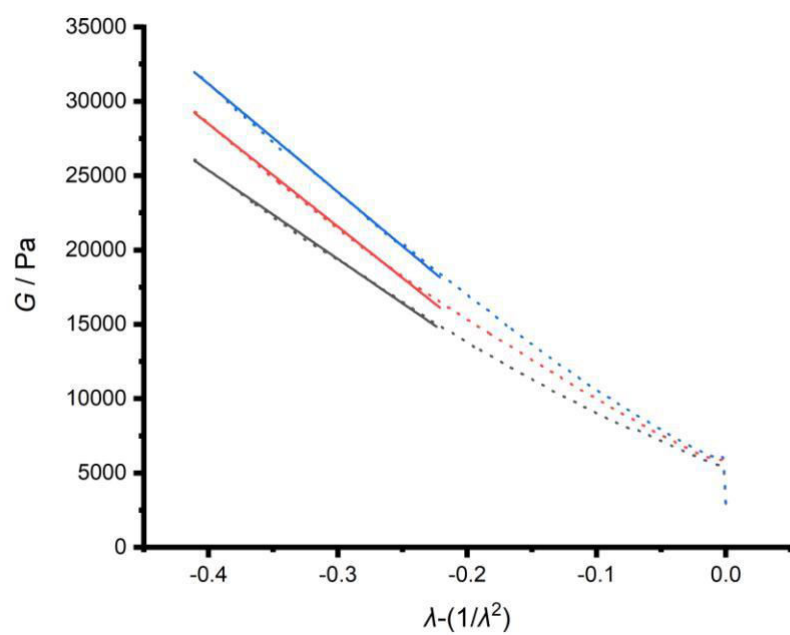


Figure F.4: The stress-strain curve of PEGDA_AMPS_50_50 hydrogel

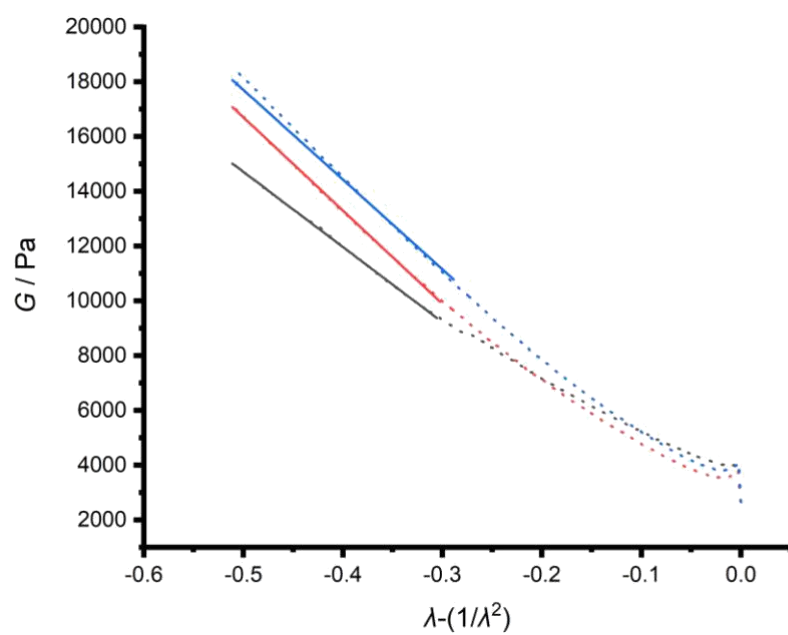


Figure F.5: The stress-strain curve of PEGDA_AMPS_60_40 hydrogel

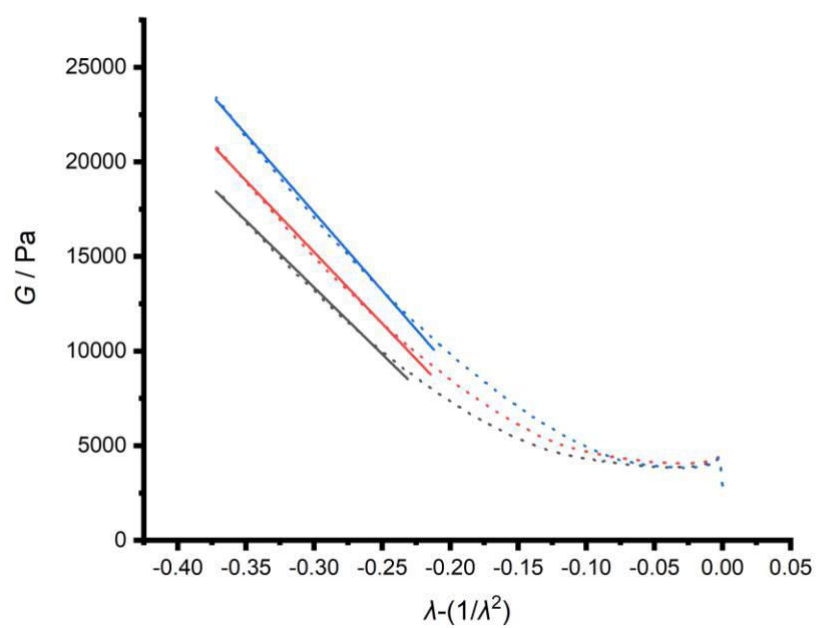


Figure F.6: The stress-strain curve of PEGDA_AMPS_70_30 hydrogel

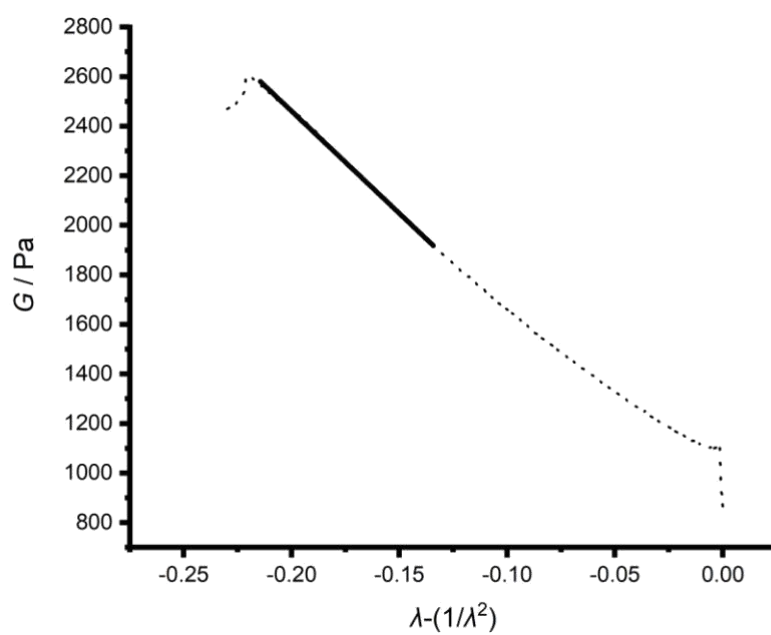


Figure F.7: The stress-strain curve of PEGDA_AMPS_80_20 hydrogel

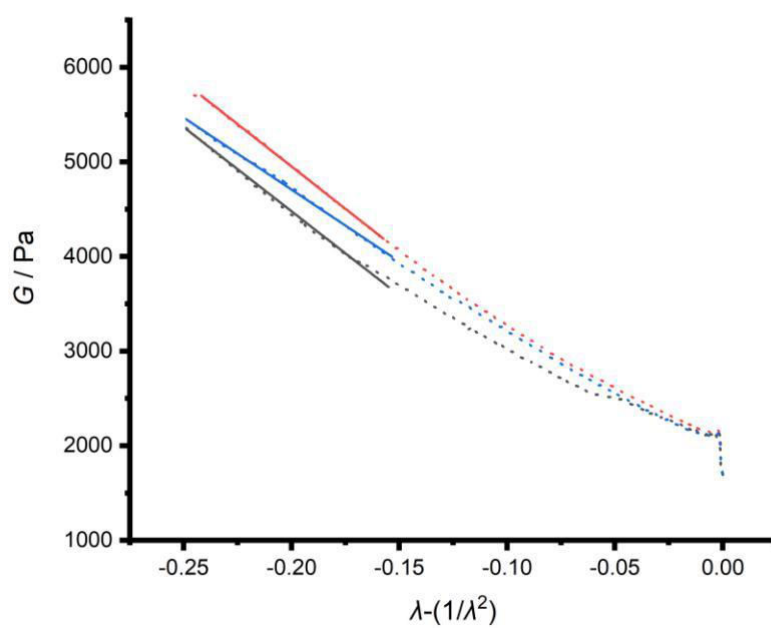


Figure F.8: The stress-strain curve of PEGDA_AMPS_90_10 hydrogel

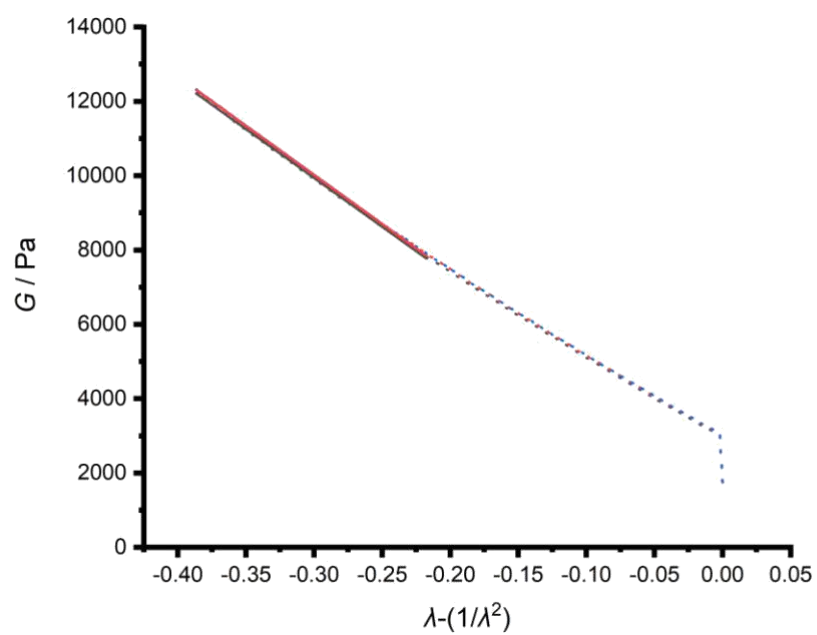


Figure F.9: The stress-strain curve of PEGDA_AMPS_100_0 hydrogel

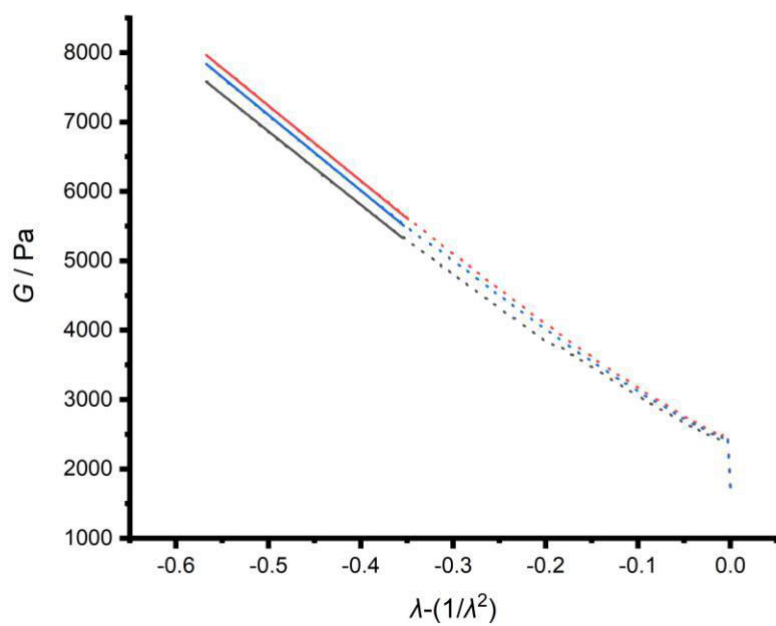


Figure F.10: The stress-strain curve of PEGDA_MPEGA_AMPS_10_10_80 hydrogel

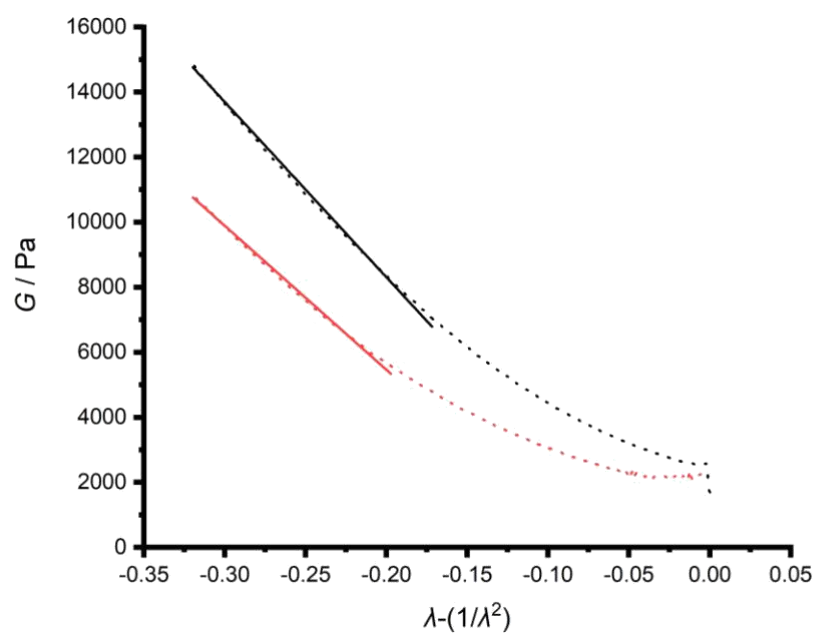


Figure F.11: The stress-strain curve of PEGDA_MPEGA_AMPS_10_30_60 hydrogel

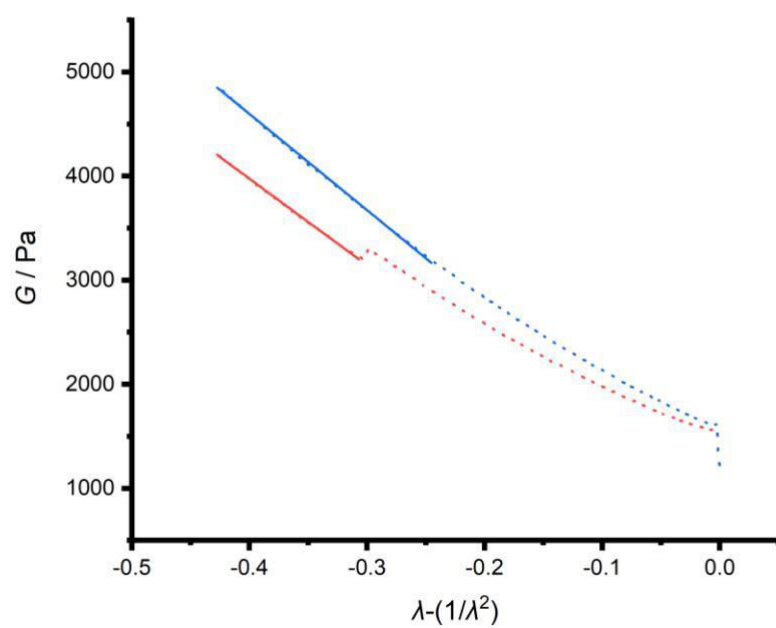


Figure F.12: The stress-strain curve of PEGDA_MPEGA_AMPS_10_45_45 hydrogel

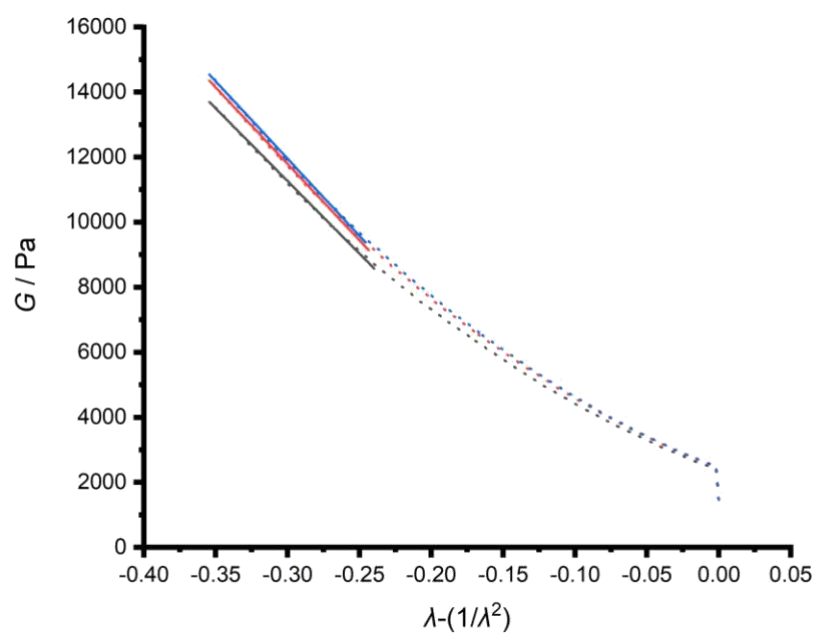


Figure F.13: The stress-strain curve of PEGDA_MPEGA_AMPS_10_60_30 hydrogel

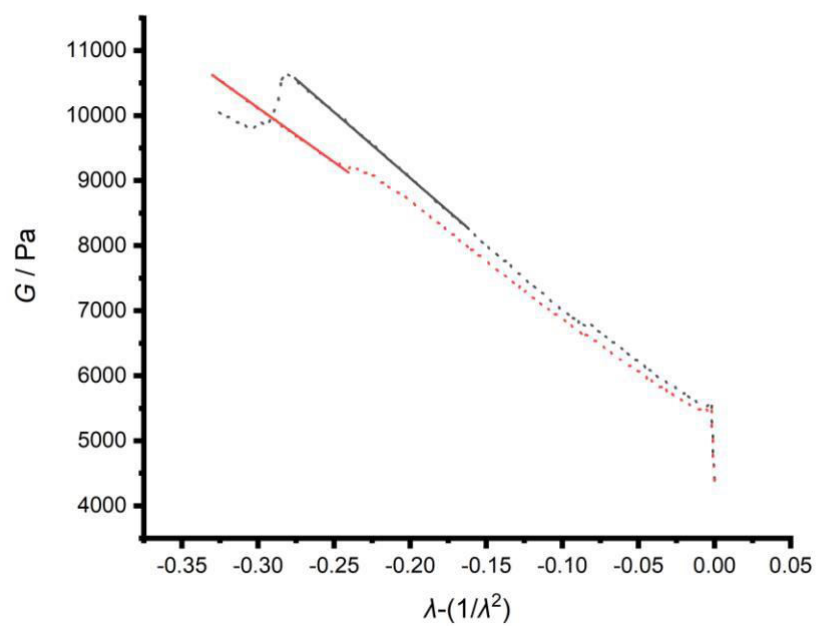


Figure F.14: The stress-strain curve of PEGDA_MPEGA_AMPS_10_80_10 hydrogel

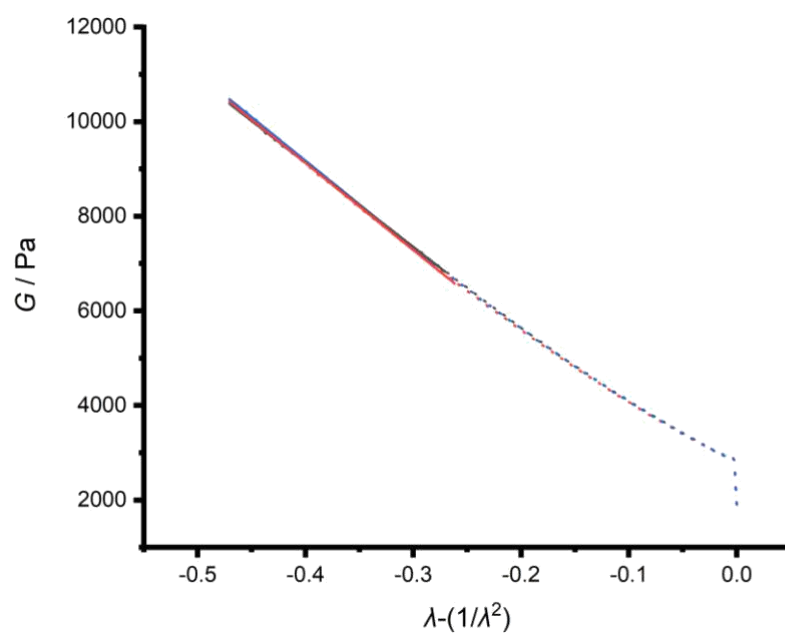


Figure F.15: The stress-strain curve of PEGDA_MPEGA_AMPS_20_10_70 hydrogel

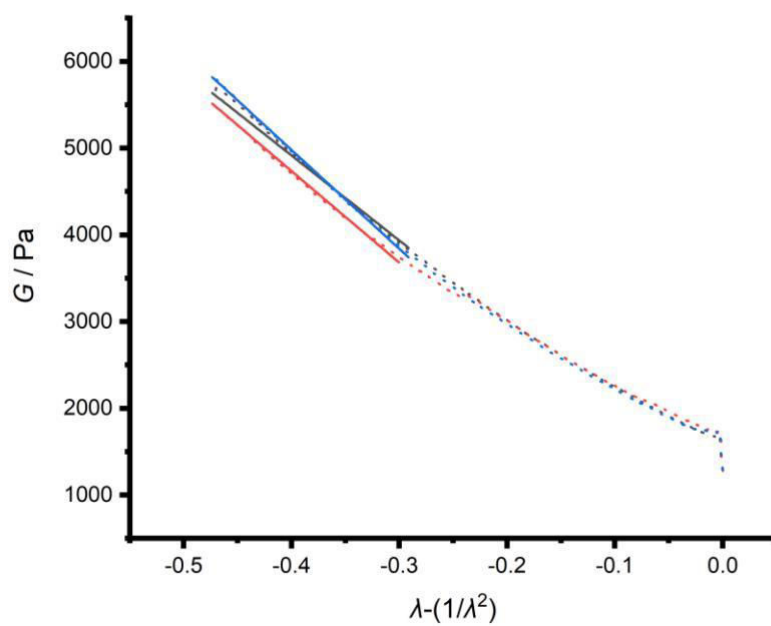


Figure F.16: The stress-strain curve of PEGDA_MPEGA_AMPS_20_30_50 hydrogel

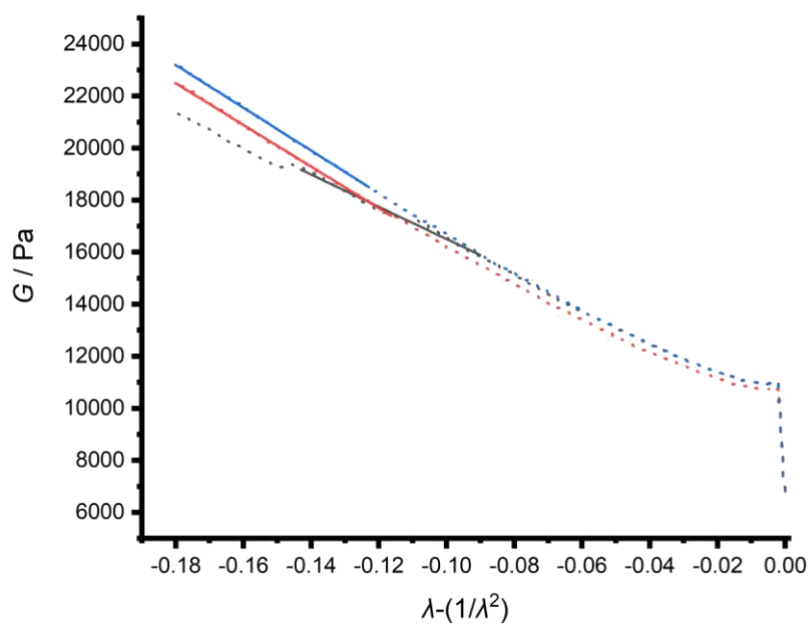


Figure F.17: The stress-strain curve of PEGDA_MPEGA_AMPS_20_40_40 hydrogel

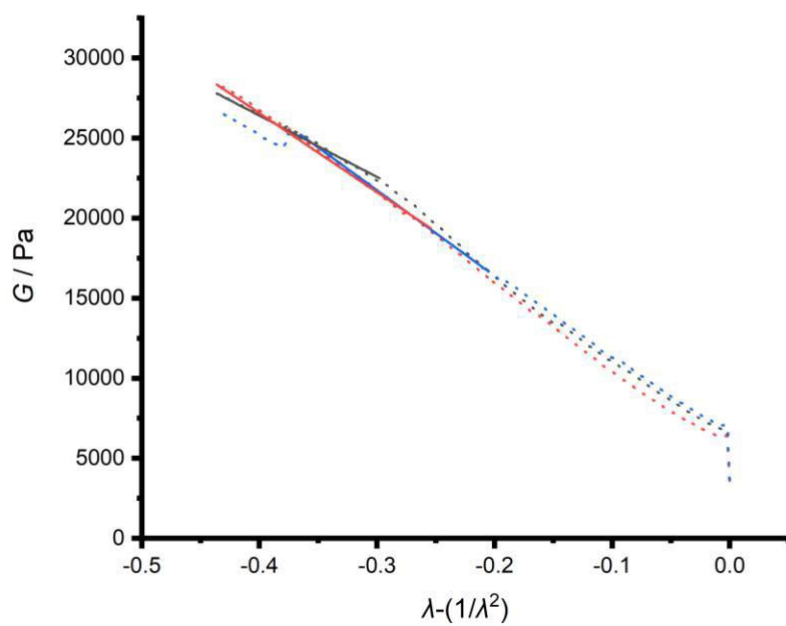


Figure F.18: The stress-strain curve of PEGDA_MPEGA_AMPS_20_50_30 hydrogel

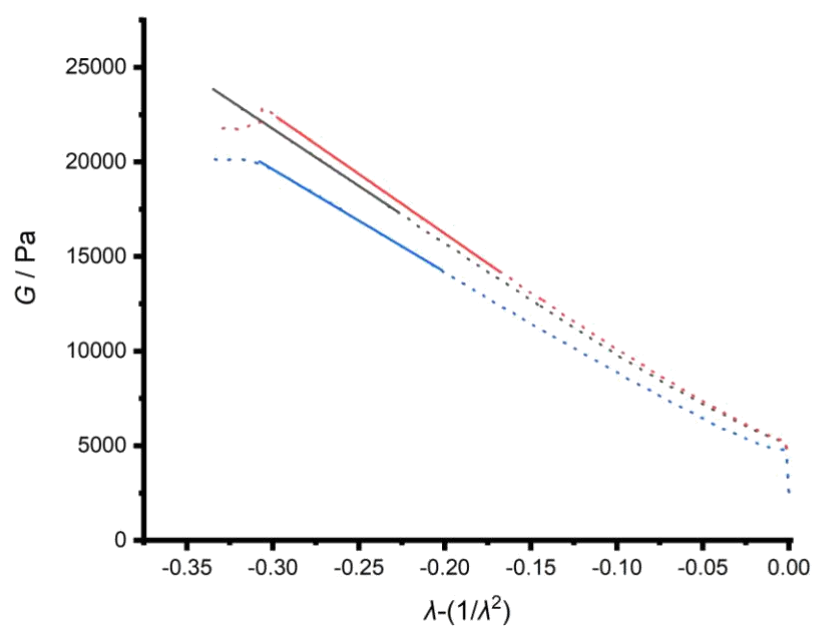


Figure F.19: The stress-strain curve of PEGDA_MPEGA_AMPS_20_70_10 hydrogel

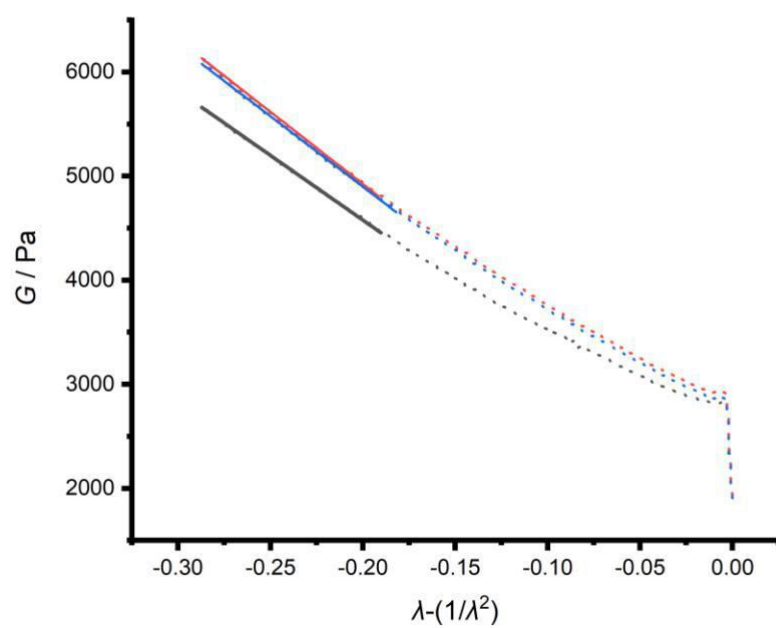


Figure F.20: The stress-strain curve of PEGDA_MPEGA_AMPS_30_10_60 hydrogel

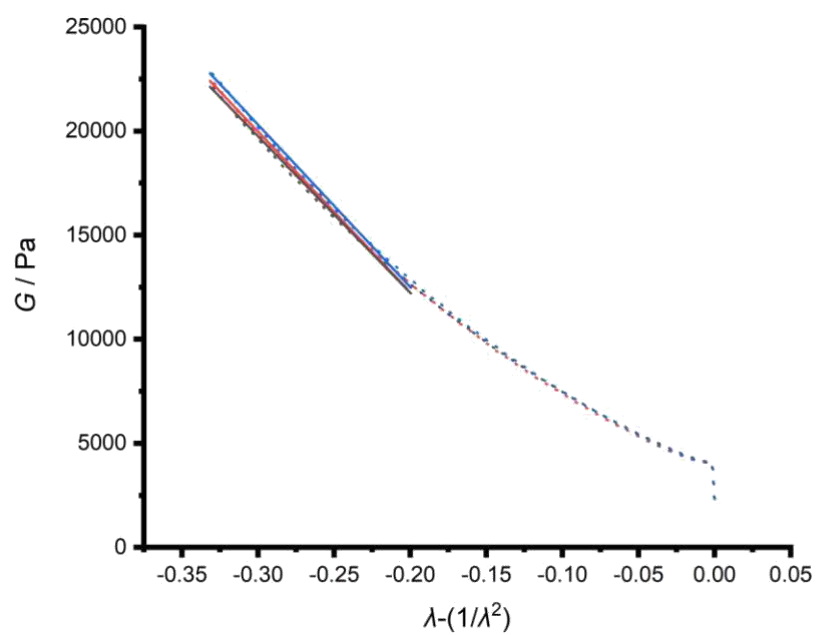
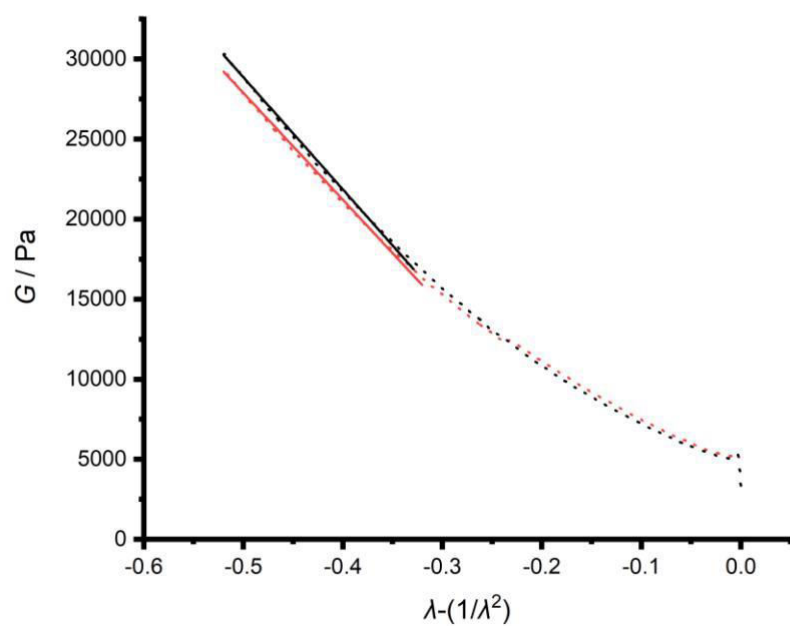


Figure F.21: The stress-strain curve of PEGDA_MPEGA_AMPS_30_20_50 hydrogel



F. Figure 22: The stress-strain curve of PEGDA_MPEGA_AMPS_30_35_35 hydrogel

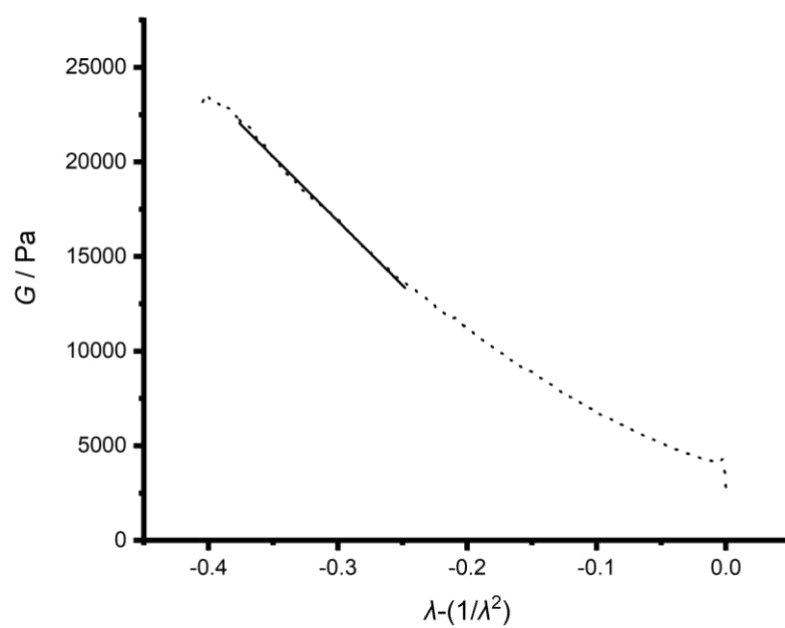


Figure F.23: The stress-strain curve of PEGDA_MPEGA_AMPS_30_50_20 hydrogel

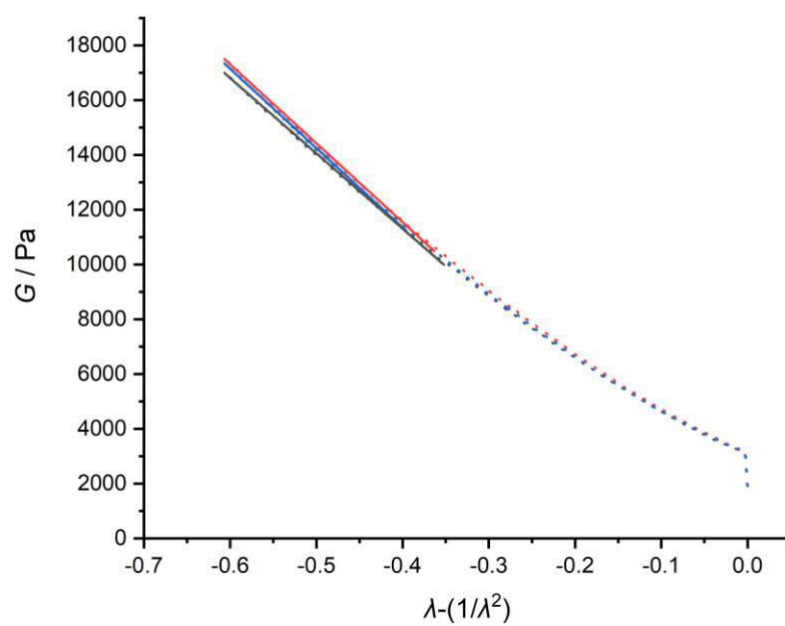


Figure F.24: The stress-strain curve of PEGDA_MPEGA_AMPS_30_60_10 hydrogel

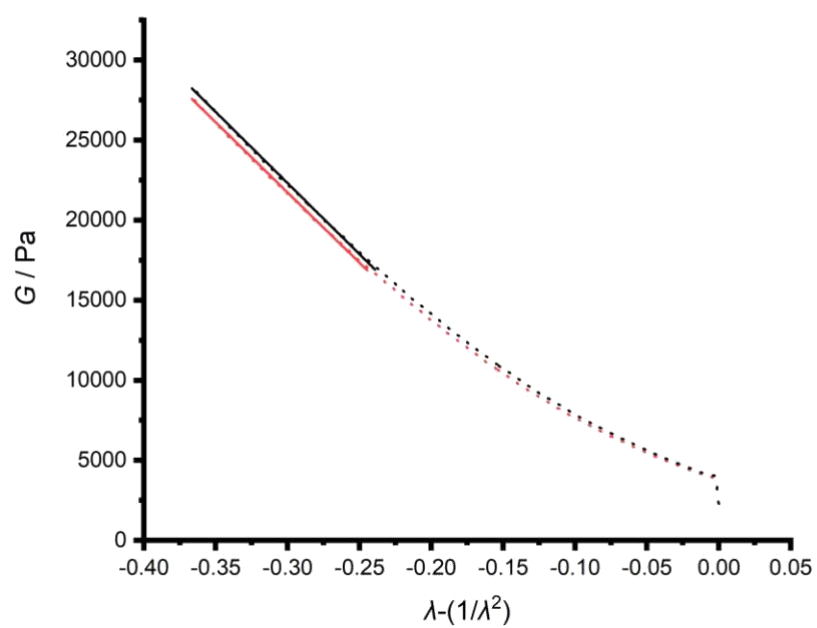


Figure F.25: The stress-strain curve of PEGDA_MPEGA_AMPS_40_10_50 hydrogel

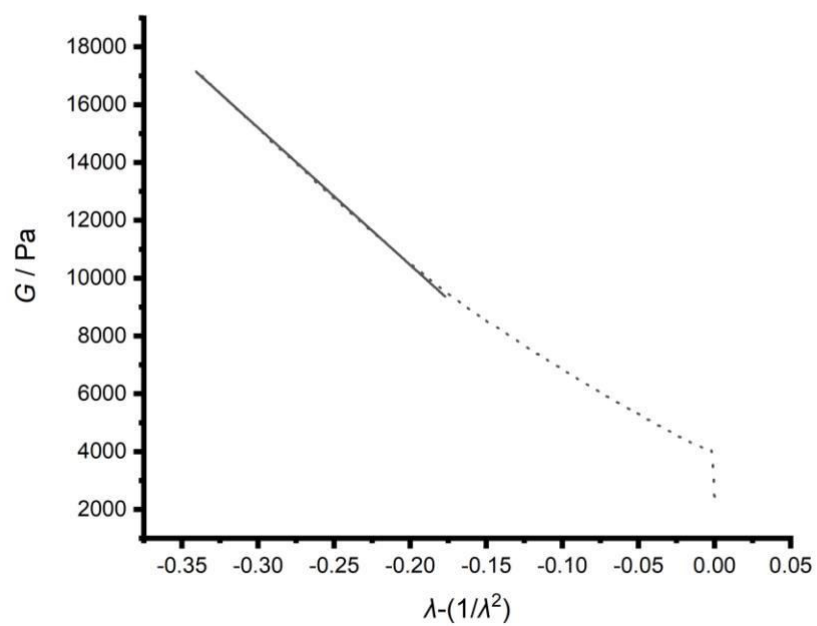


Figure F.26: The stress-strain curve of PEGDA_MPEGA_AMPS_40_20_40 hydrogel

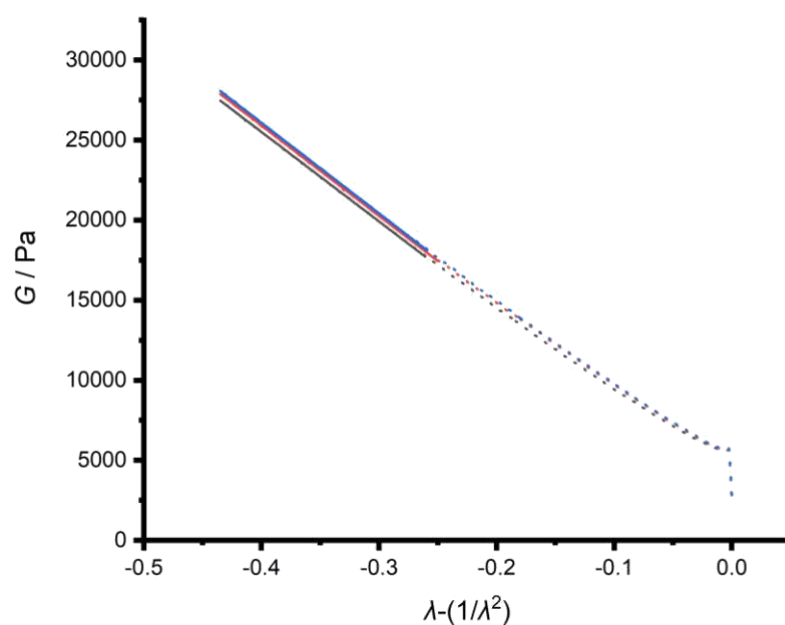


Figure F.27: The stress-strain curve of PEGDA_MPEGA_AMPS_40_30_30 hydrogel

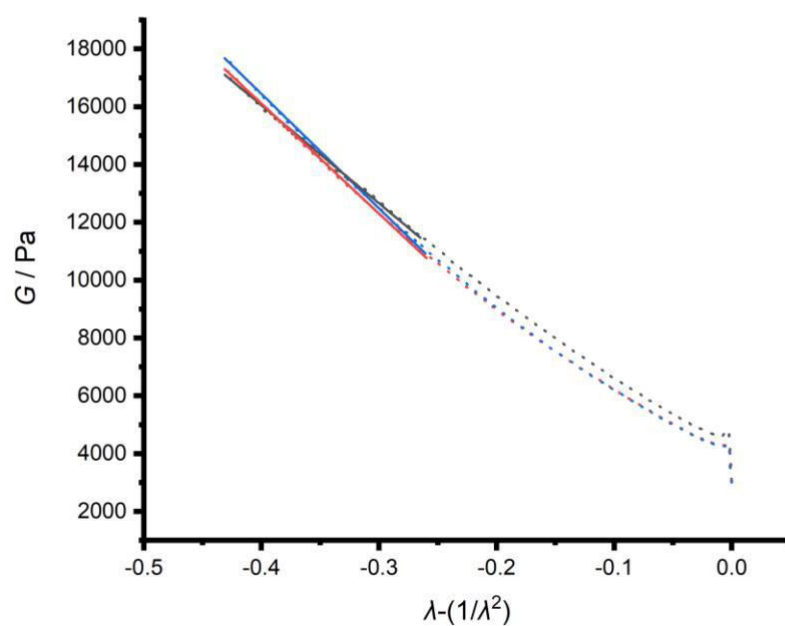


Figure F.28: The stress-strain curve of PEGDA_MPEGA_AMPS_40_40_20 hydrogel

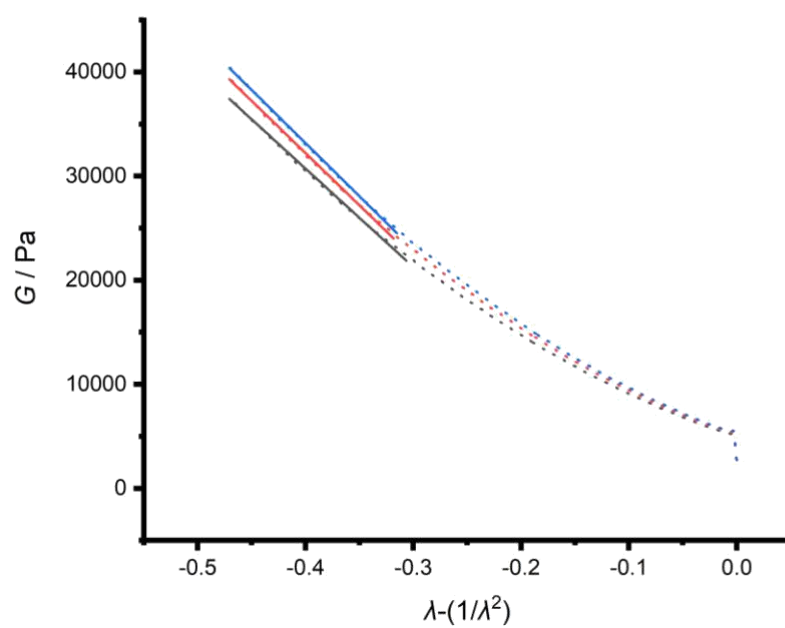


Figure F.29: The stress-strain curve of PEGDA_MPEGA_AMPS_40_50_10 hydrogel

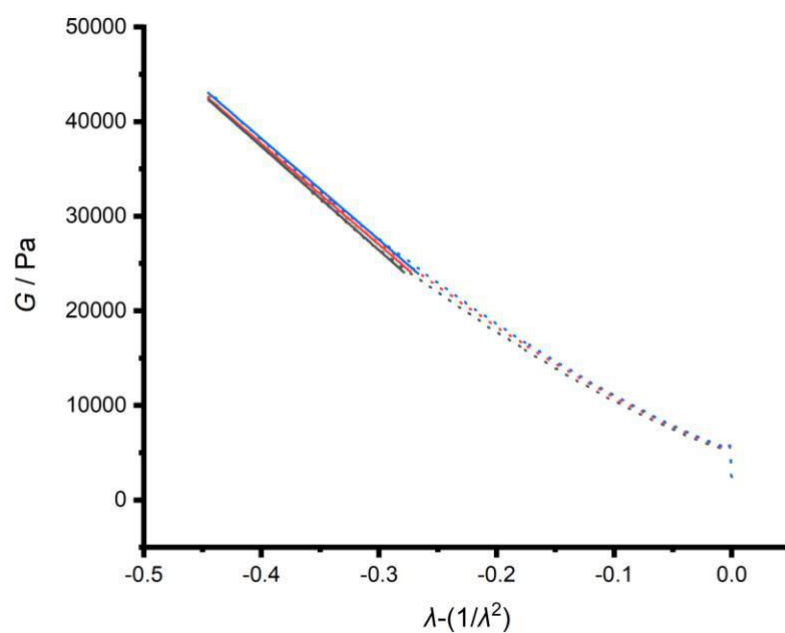


Figure F.30: The stress-strain curve of PEGDA_MPEGA_AMPS_50_5_45 hydrogel

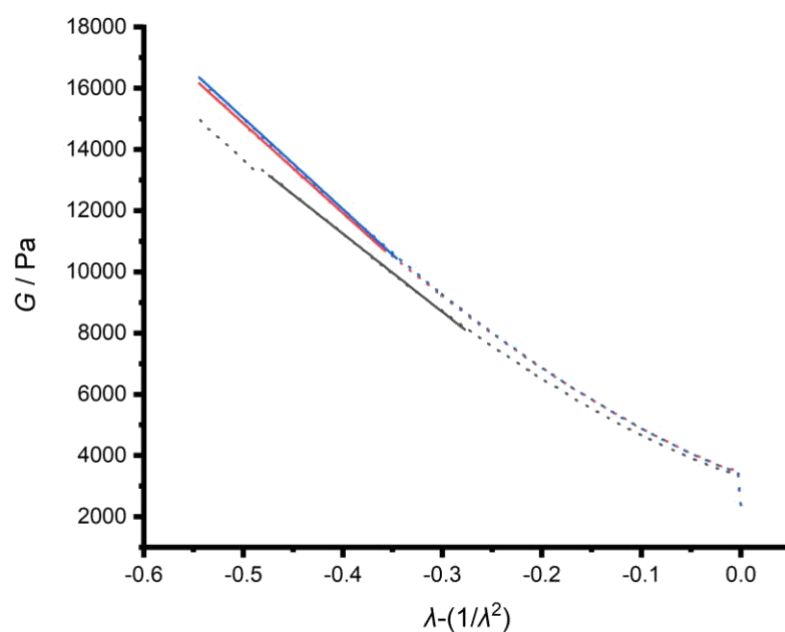


Figure F.31: The stress-strain curve of PEGDA_MPEGA_AMPS_50_15_35 hydrogel

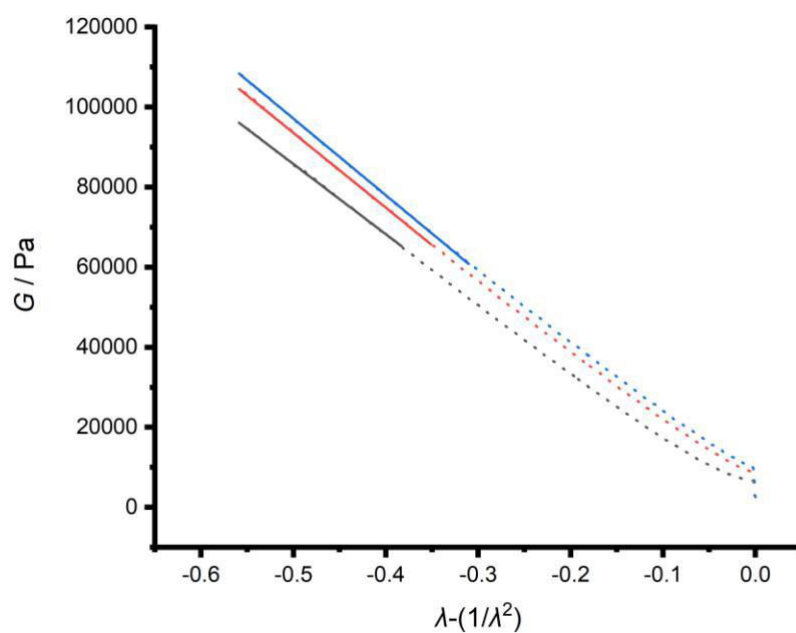


Figure F.32: The stress-strain curve of PEGDA_MPEGA_AMPS_50_25_25 hydrogel

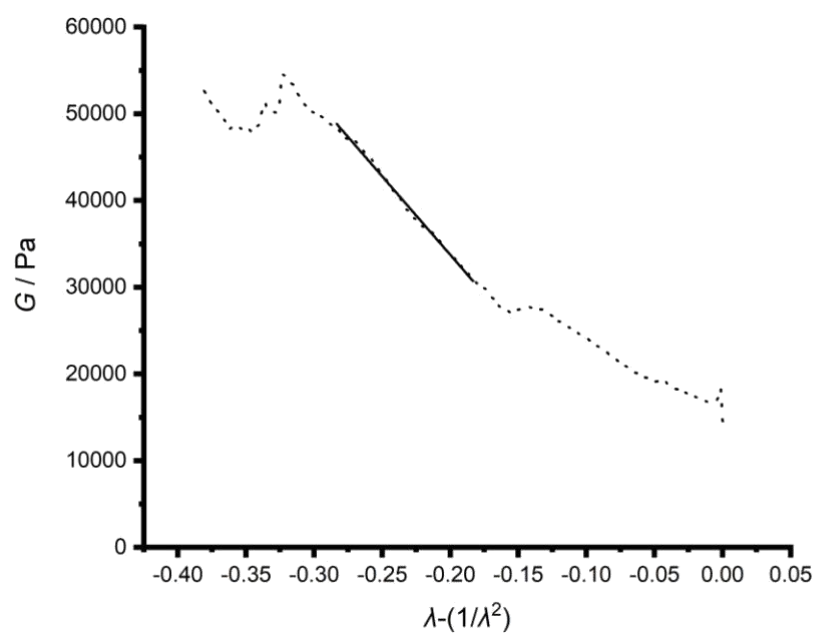


Figure F.33: The stress-strain curve of PEGDA_MPEGA_AMPS_50_35_15 hydrogel

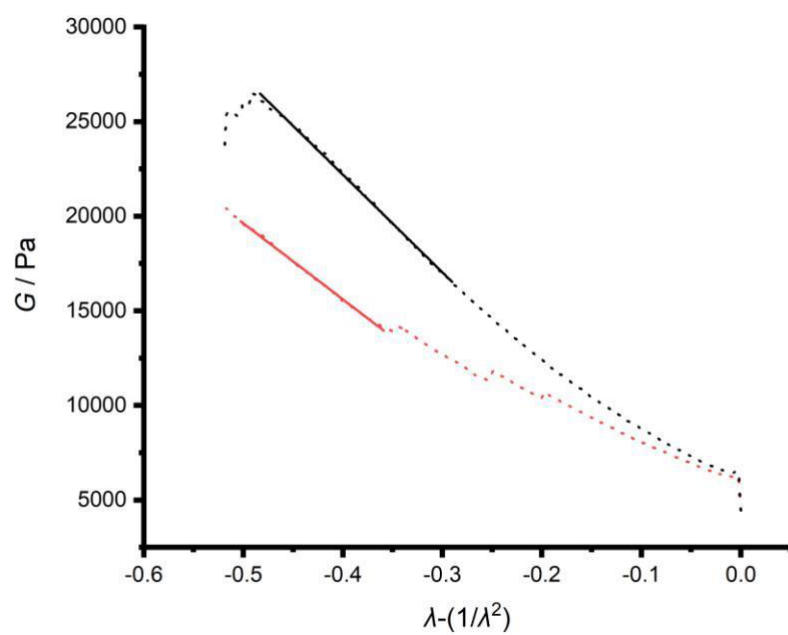


Figure F.34: The stress-strain curve of PEGDA_MPEGA_AMPS_50_45_4 hydrogel

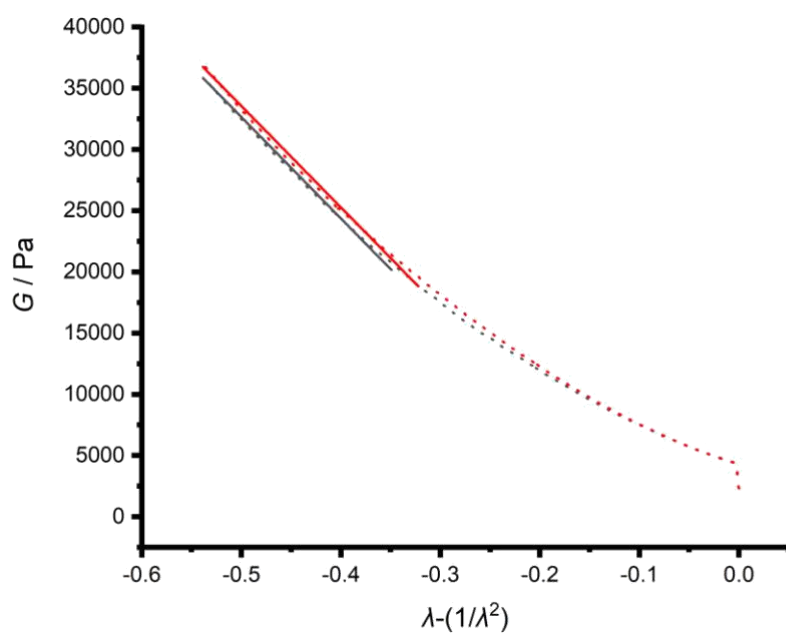


Figure F.35: The stress-strain curve of PEGDA_MPEGA_AMPS_60_10_30 hydrogel

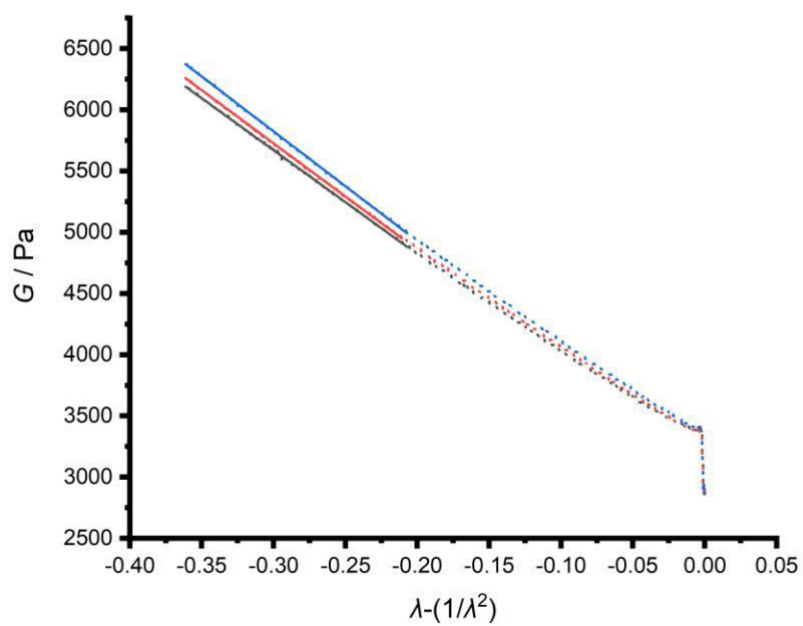


Figure F.36: The stress-strain curve of PEGDA_MPEGA_AMPS_60_15_25 hydrogel

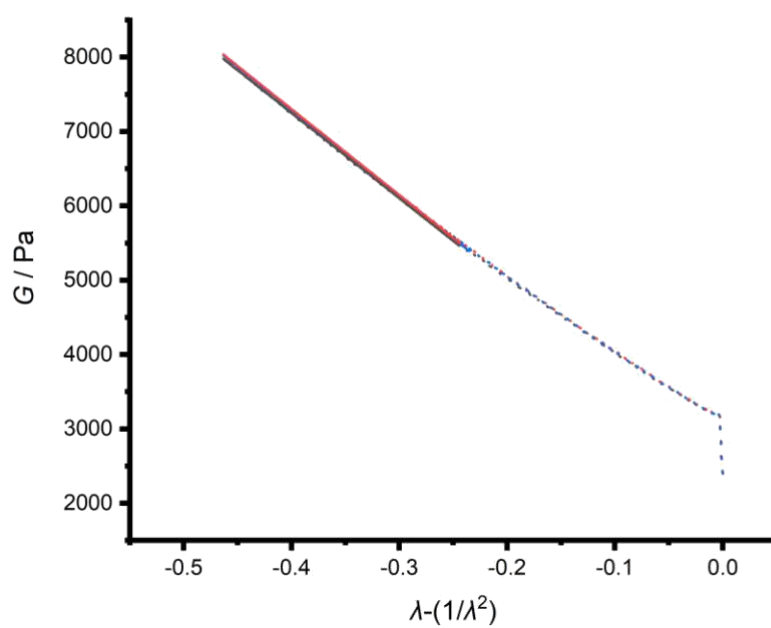


Figure F.37: The stress-strain curve of PEGDA_MPEGA_AMPS_60_20_20 hydrogel

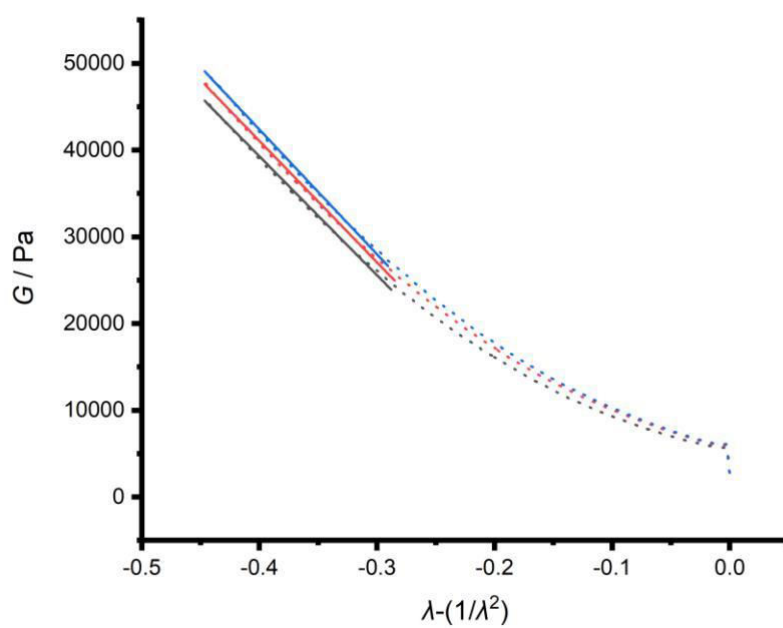


Figure F.38: The stress-strain curve of PEGDA_MPEGA_AMPS_60_25_15 hydrogel

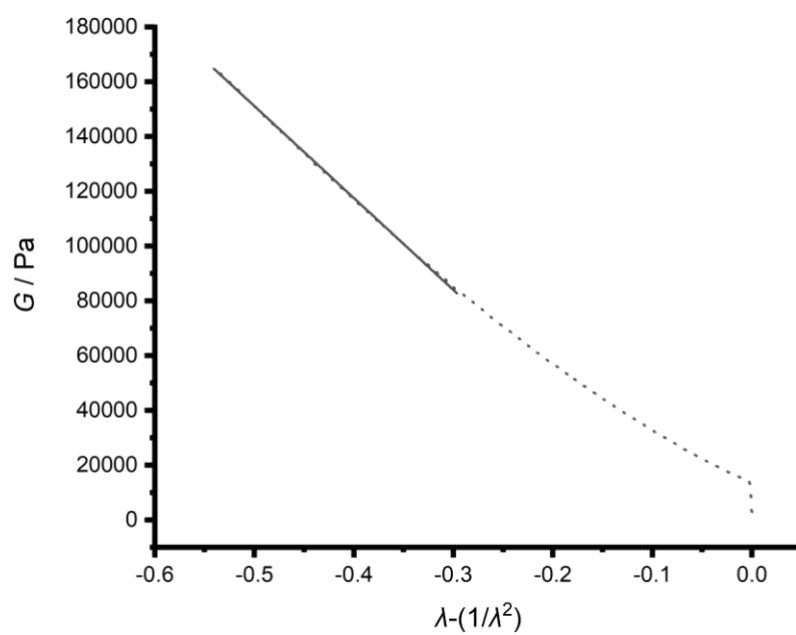


Figure F.39: The stress-strain curve of PEGDA_MPEGA_AMPS_60_30_10 hydrogel

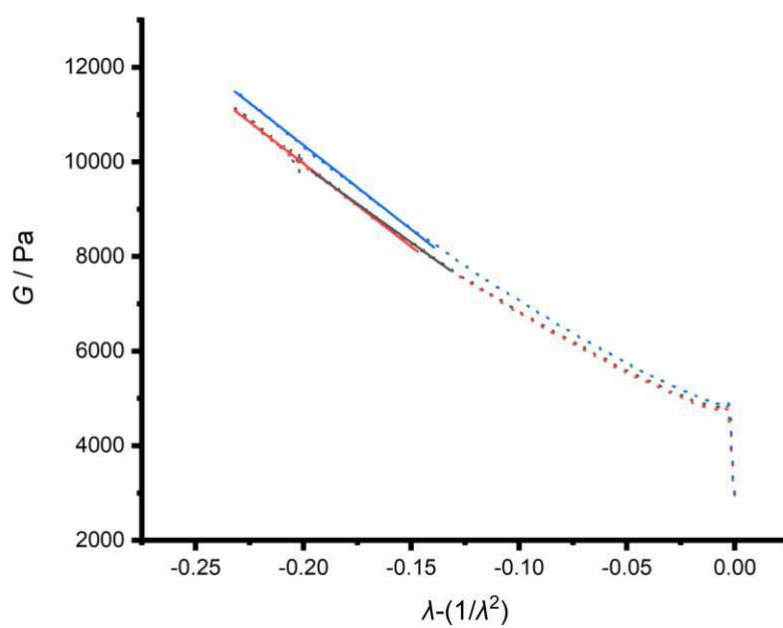


Figure F.40: The stress-strain curve of PEGDA_MPEGA_AMPS_70_5_25 hydrogel

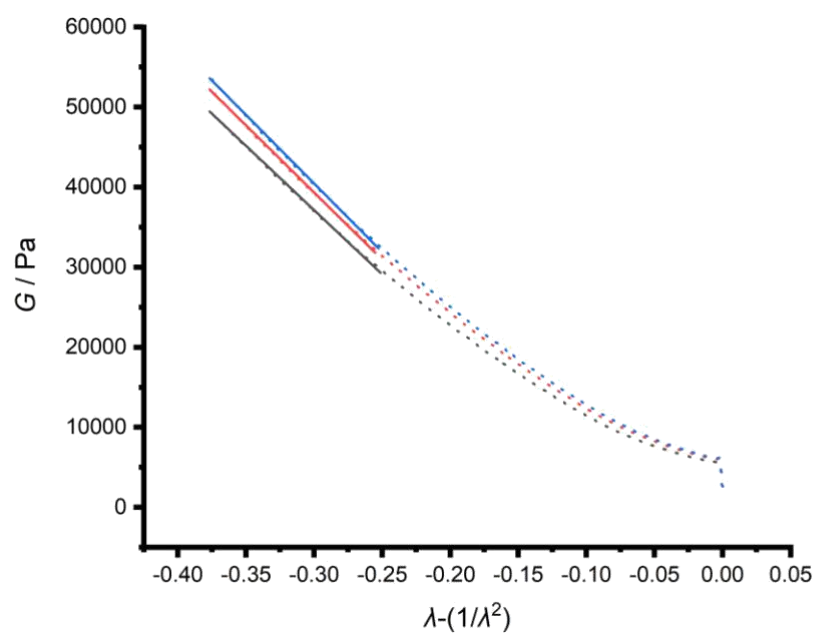


Figure F.41: The stress-strain curve of PEGDA_MPEGA_AMPS_70_10_20 hydrogel

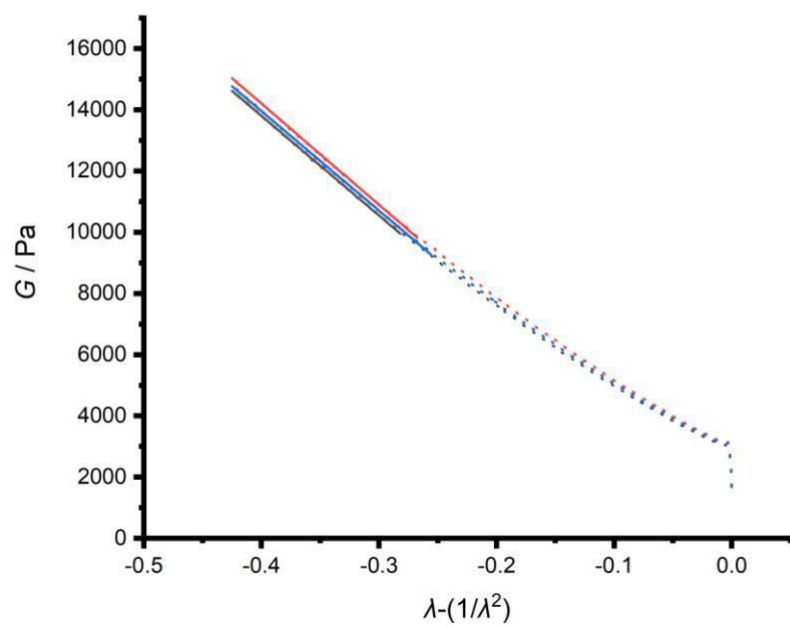


Figure F.42: The stress-strain curve of PEGDA_MPEGA_AMPS_70_15_15 hydrogel

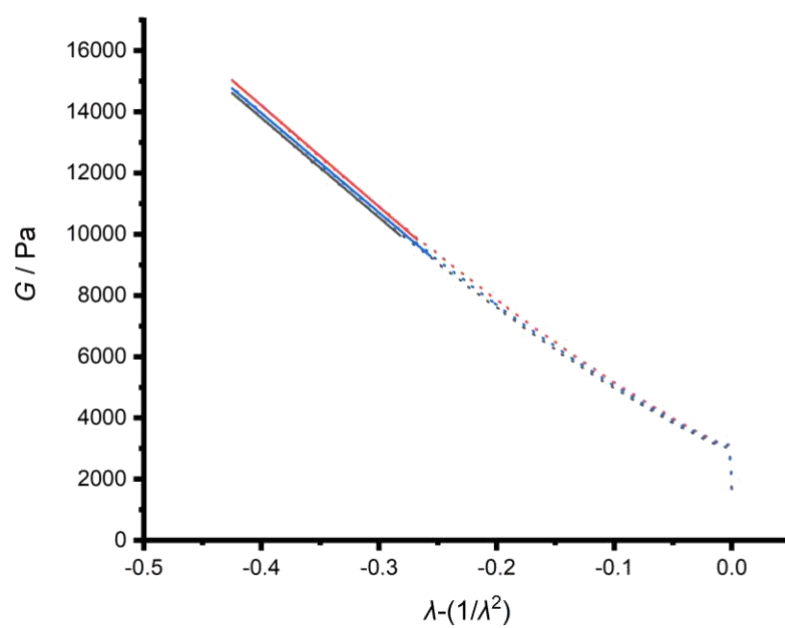


Figure F.43: The stress-strain curve of PEGDA_MPEGA_AMPS_70_20_10 hydrogel

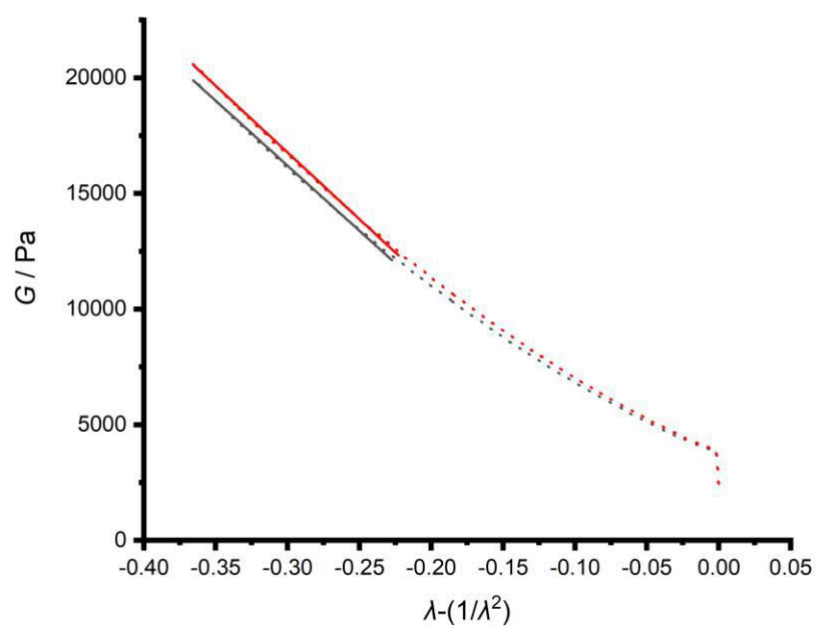


Figure F.44: The stress-strain curve of PEGDA_MPEGA_AMPS_70_25_5 hydrogel

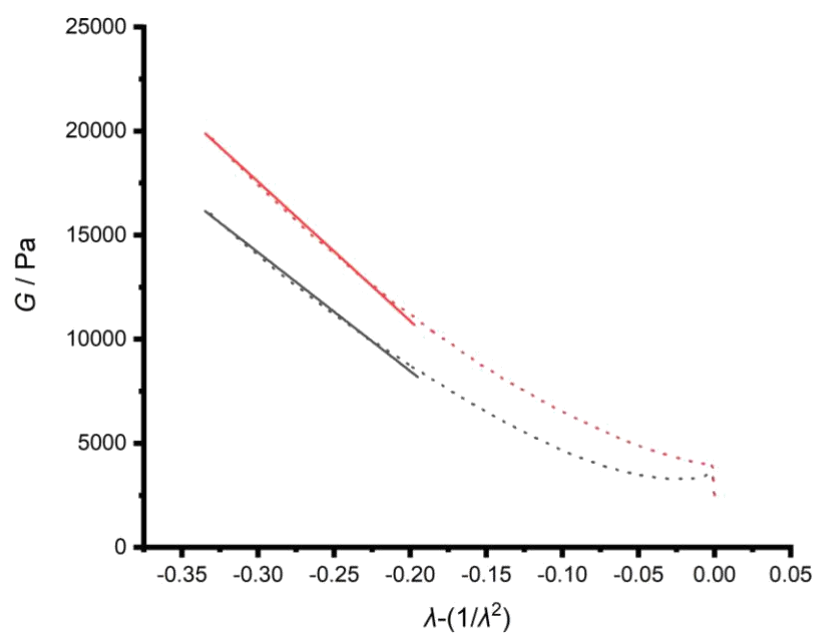


Figure F.45: The stress-strain curve of PEGDA_MPEGA_AMPS_80_4_16 hydrogel

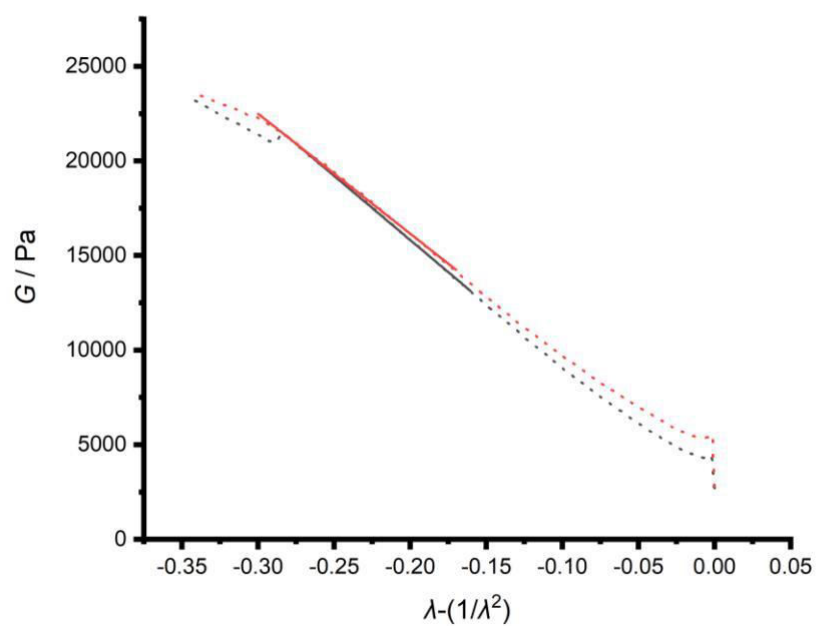


Figure F.46: The stress-strain curve of PEGDA_MPEGA_AMPS_80_7_13 hydrogel

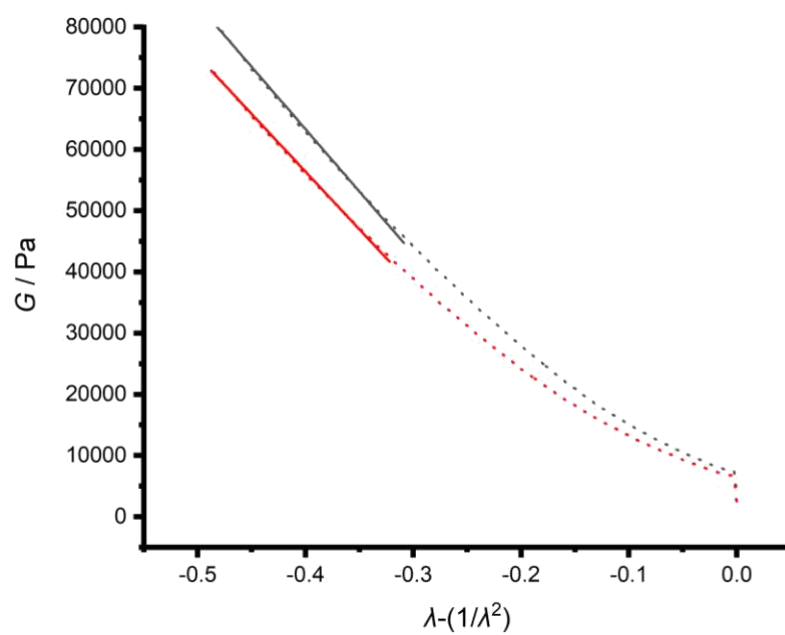


Figure F.47: The stress-strain curve of PEGDA_MPEGA_AMPS_80_10_10 hydrogel

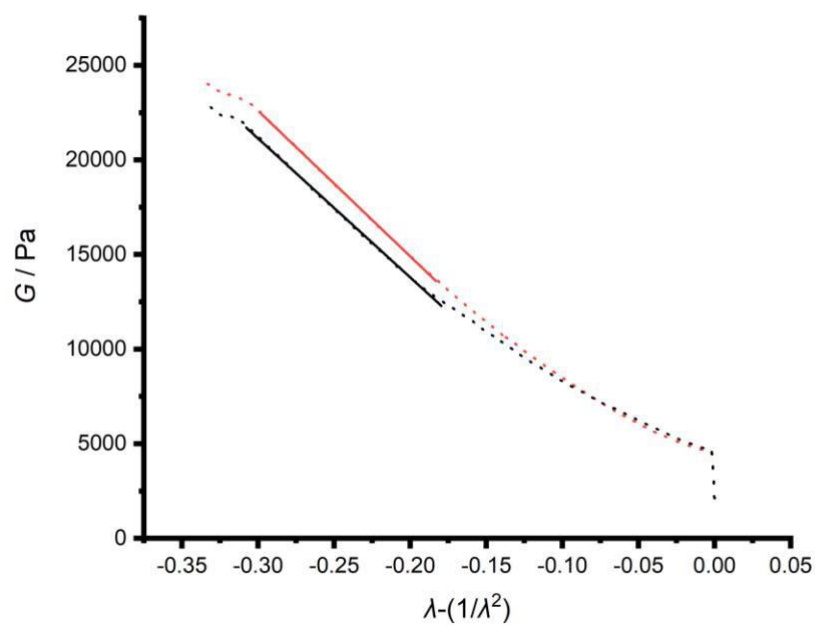


Figure F.48: The stress-strain curve of PEGDA_MPEGA_AMPS_80_13_7 hydrogel

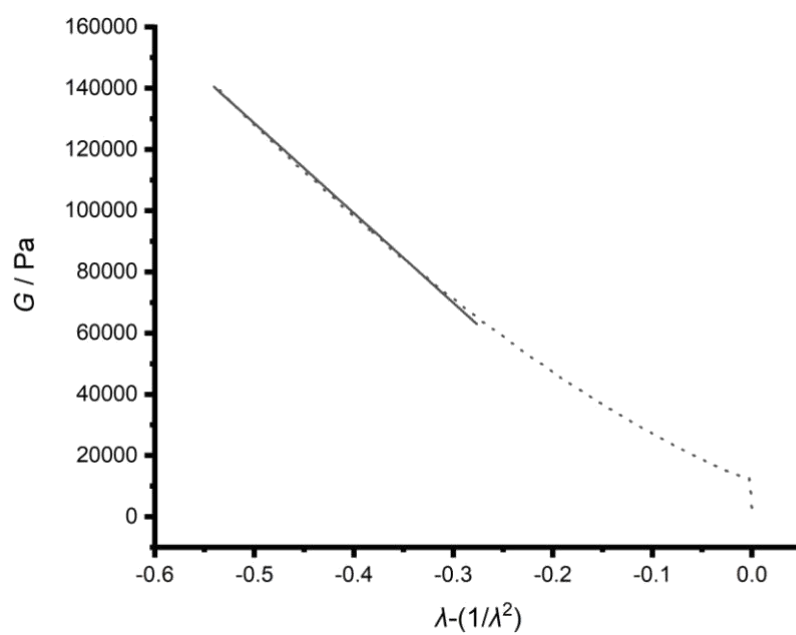


Figure F.49: The stress-strain curve of PEGDA_MPEGA_AMPS_80_16_4 hydrogel

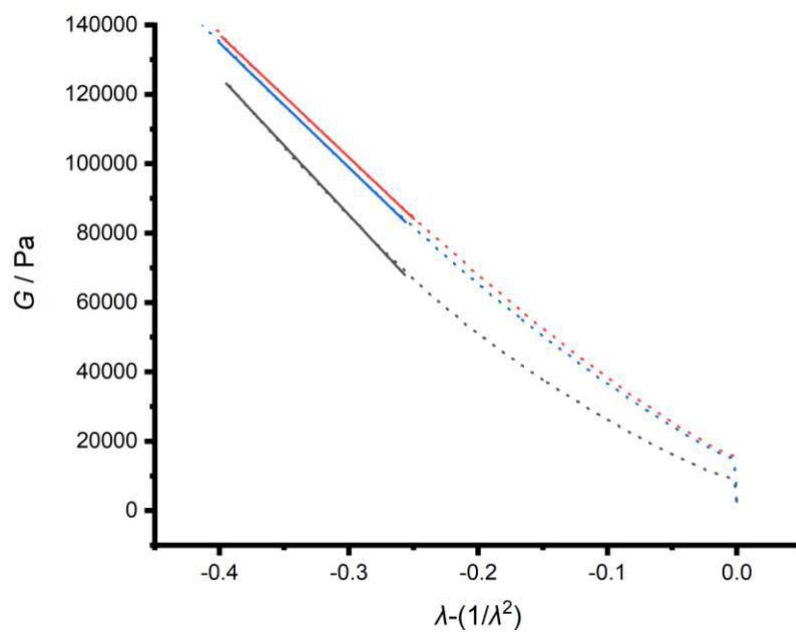


Figure F.50: The stress-strain curve of PEGDA_MPEGA_AMPS_90_1_9 hydrogel

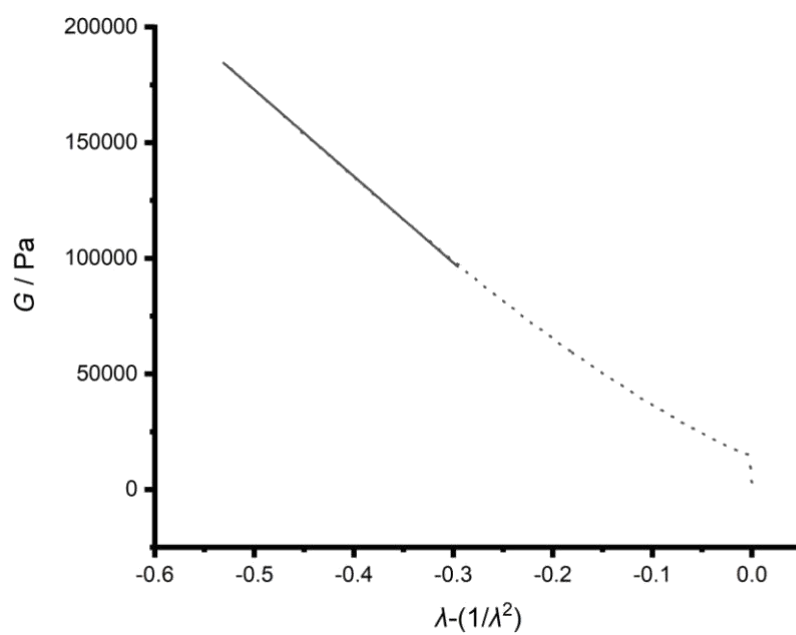


Figure F.51: The stress-strain curve of PEGDA_MPEGA_AMPS_90_3_7 hydrogel

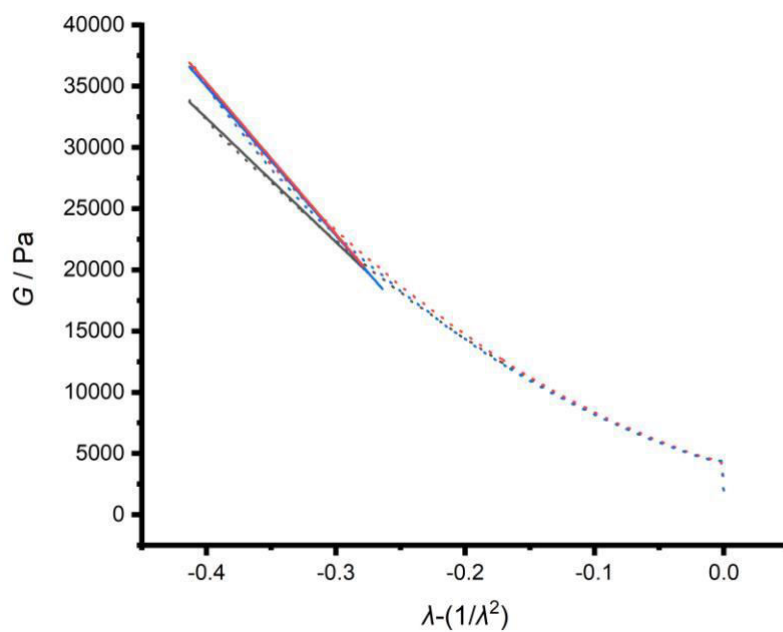


Figure F.52: The stress-strain curve of PEGDA_MPEGA_AMPS_90_5_5 hydrogel

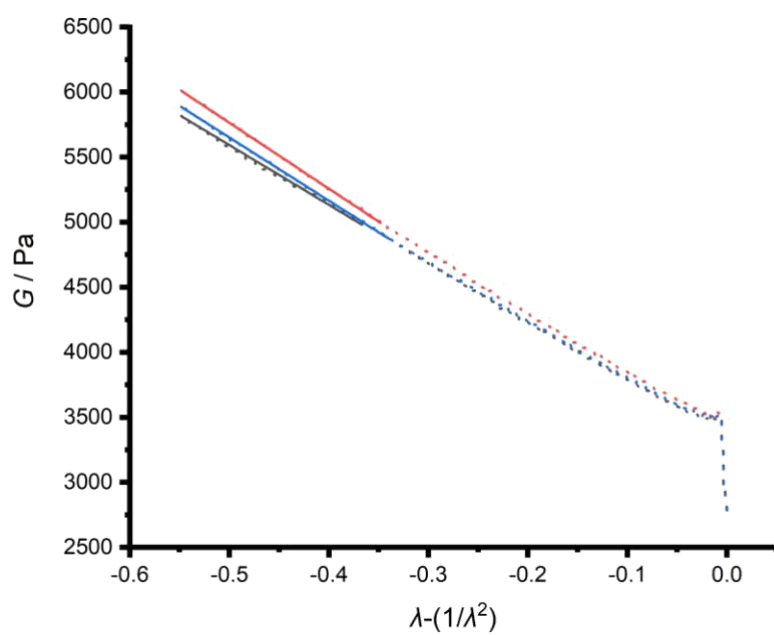


Figure F.53: The stress-strain curve of PEGDA_MPEGA_AMPS_90_7_3 hydrogel

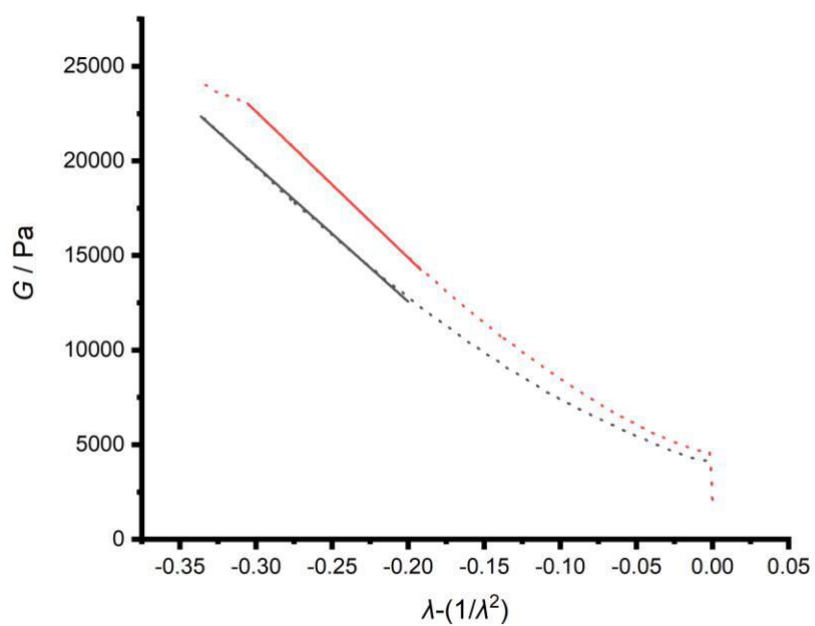


Figure F.54: The stress-strain curve of PEGDA_MPEGA_AMPS_90_9_1 hydrogel

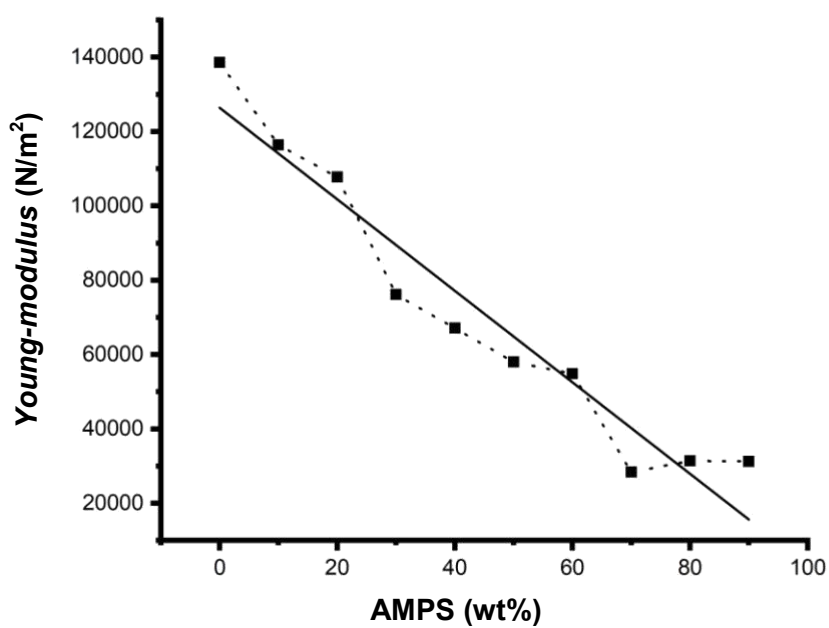


Figure F.55: Young's modulus of PEGDA-AMPS hydrogels as a function of the AMPS content

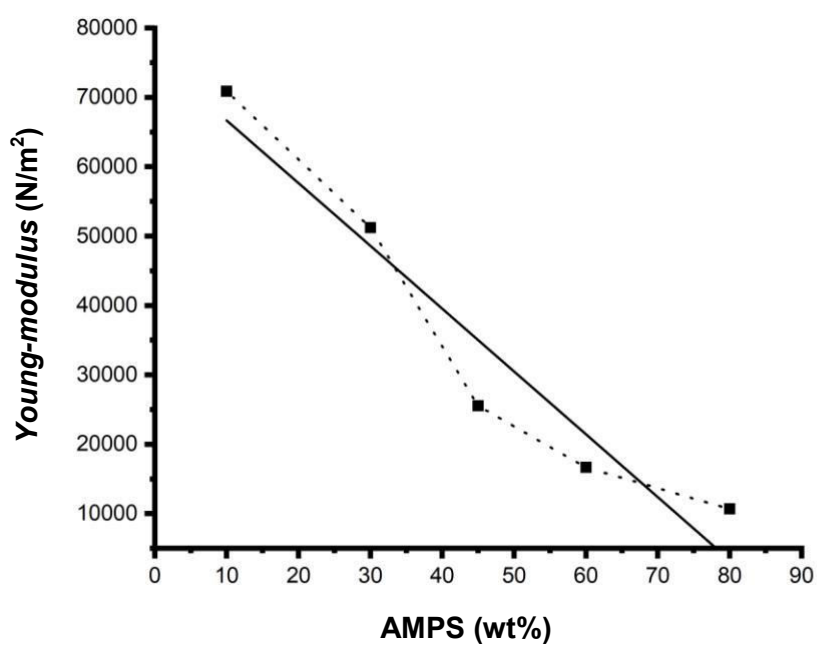


Figure F.56: Young's modulus of 10% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS content

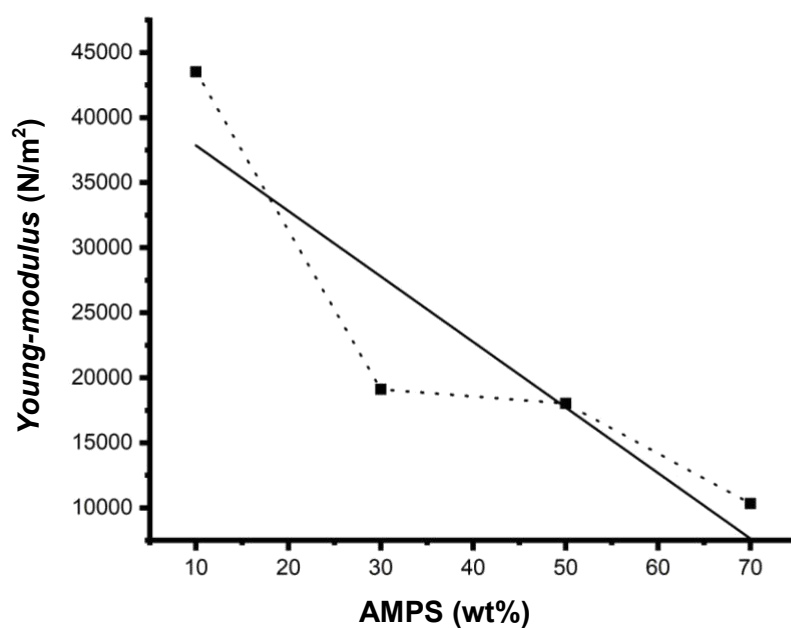


Figure F.57: Young's modulus of 20% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS content

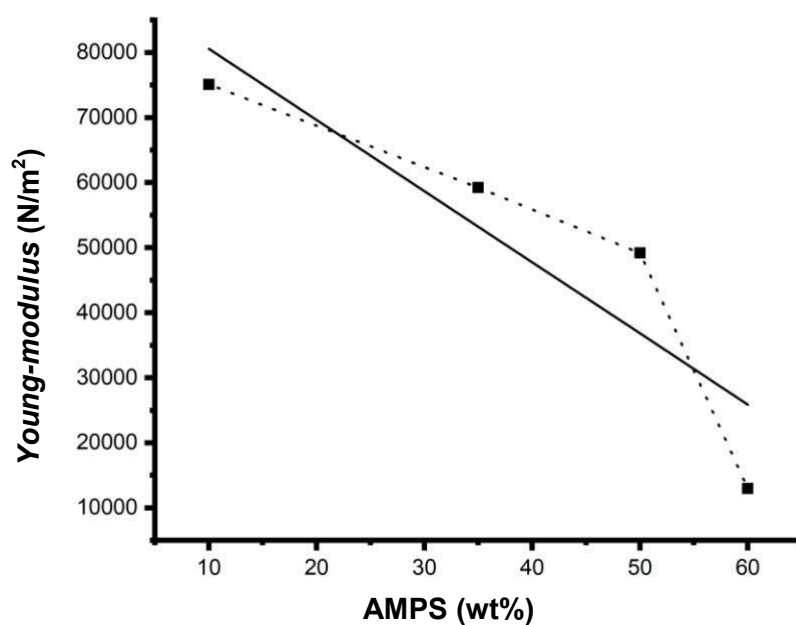


Figure F.58: Young's modulus of 30% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS content

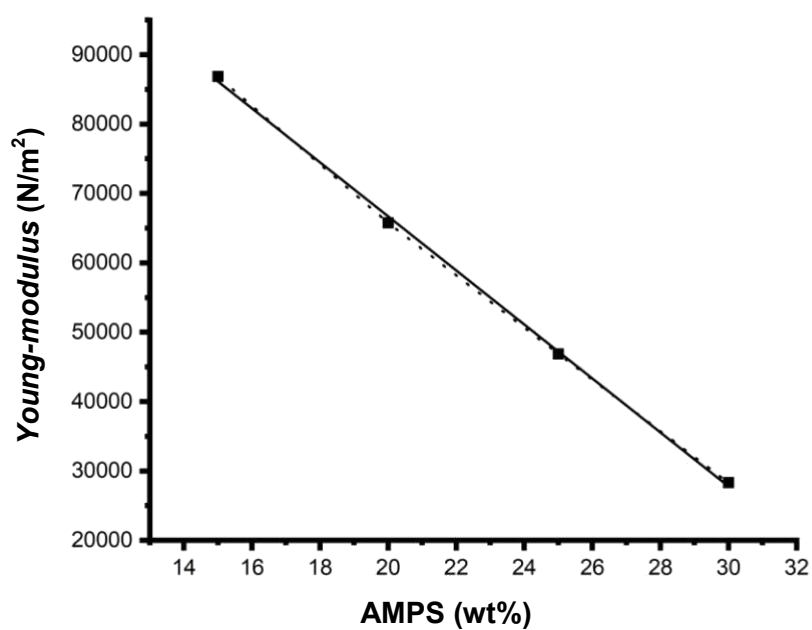


Figure F.59: Young's modulus of 40% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

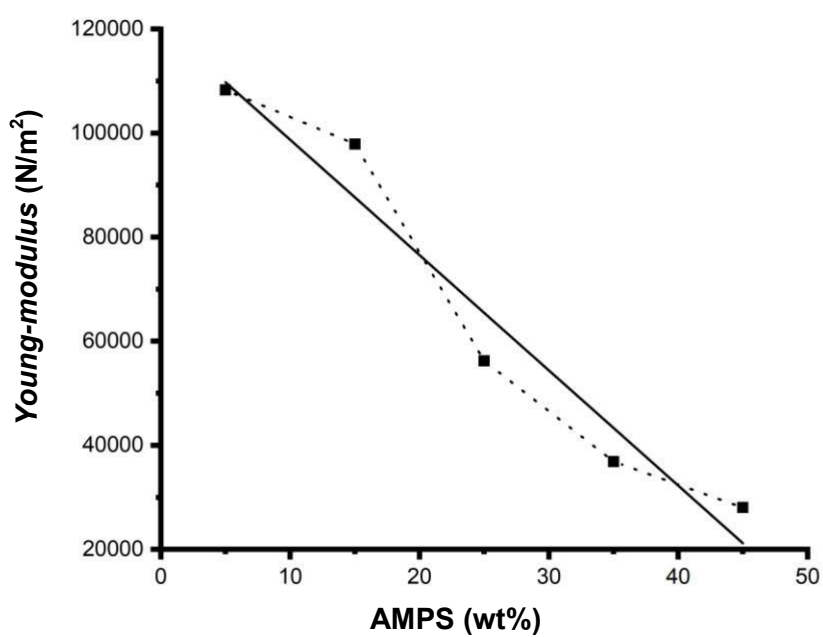


Figure F.60: Young's modulus of 50% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

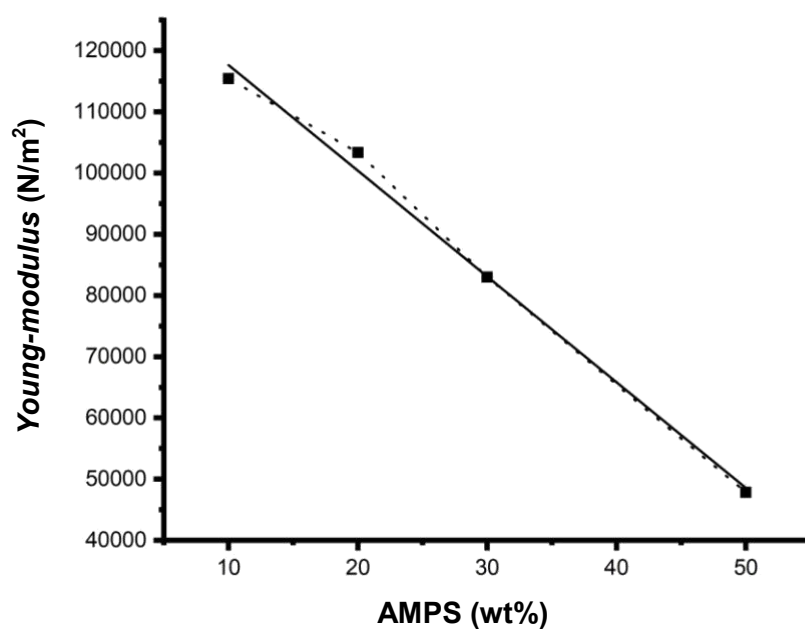


Figure F.61: Young's modulus of 60% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

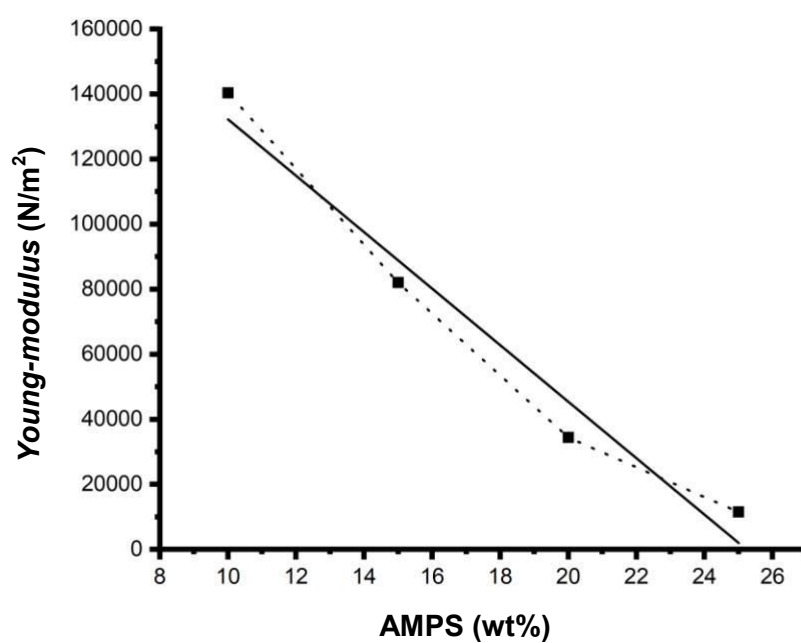


Figure F.62: Young's modulus of 70% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

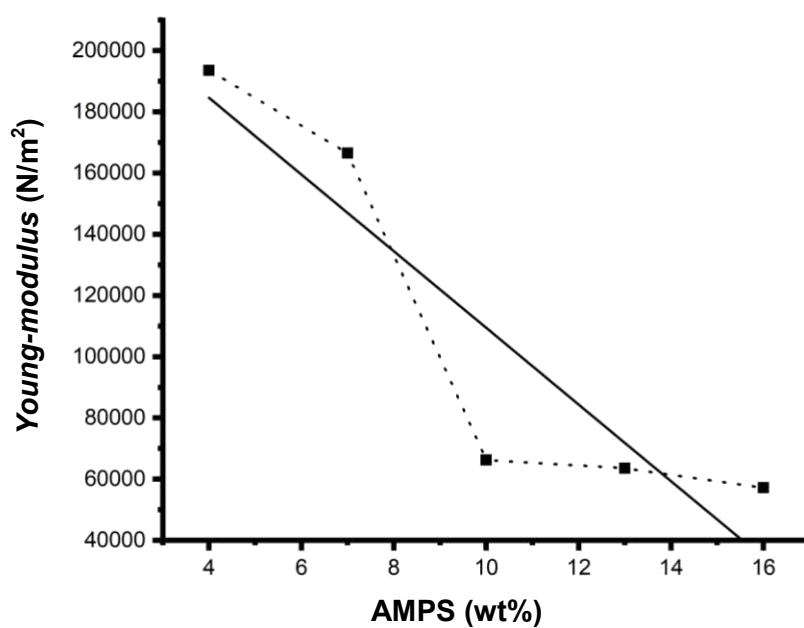


Figure F.63: Young's modulus of 80% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

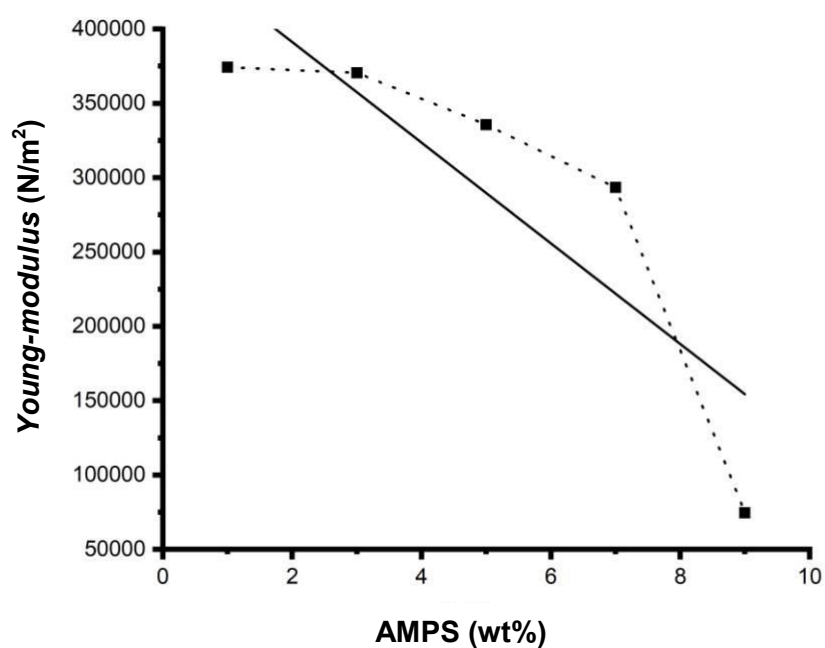


Figure F.64: Young's modulus of 90% PEGDA-MPEGA-AMPS hydrogels as a function of the AMPS

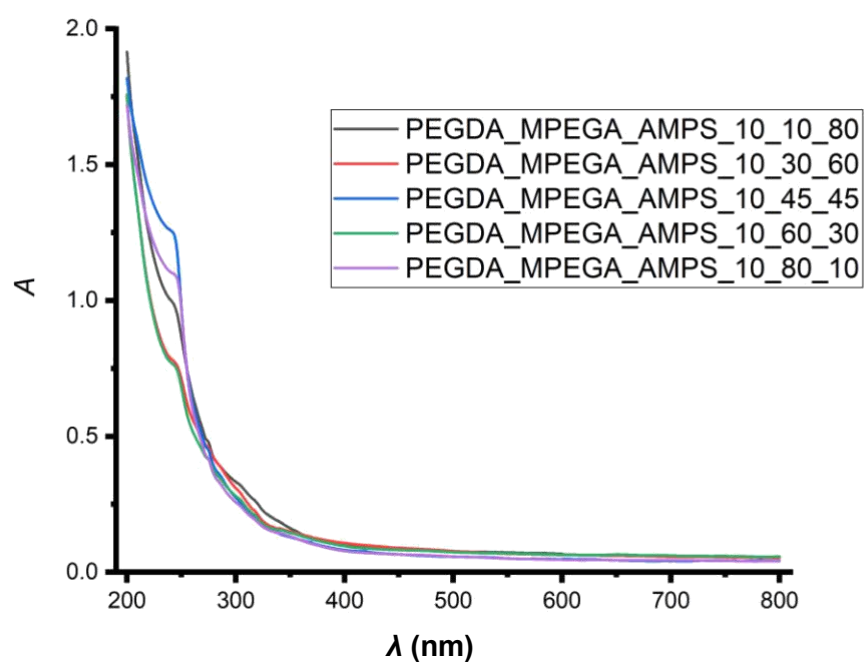


Figure F.65: Absorbance of 10% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

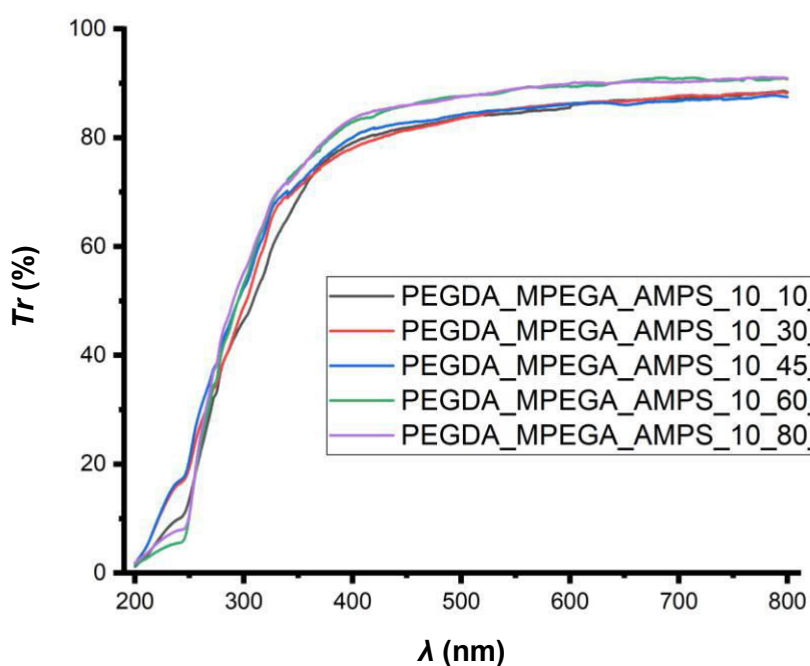


Figure F.66: Transmittance of 10% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

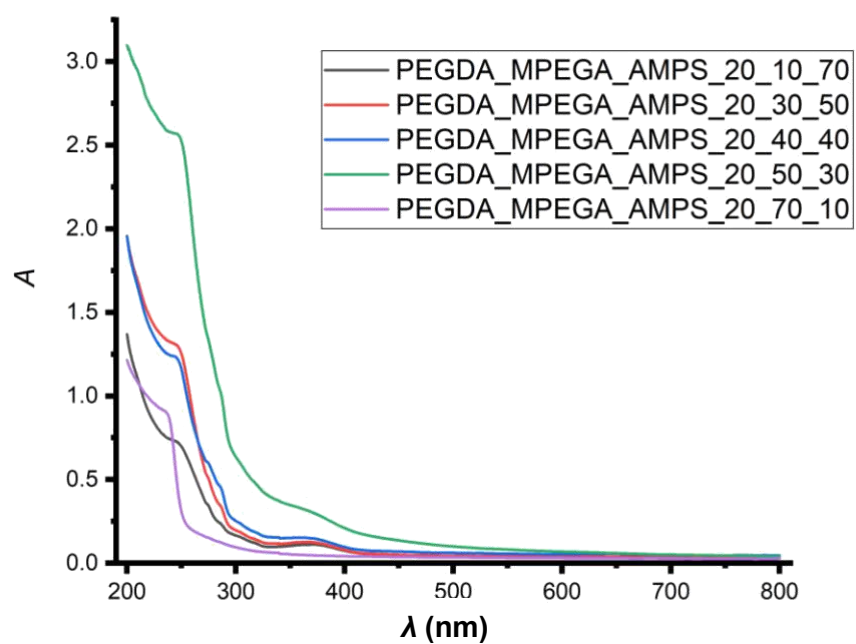


Figure F.67: Absorbance of 20% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

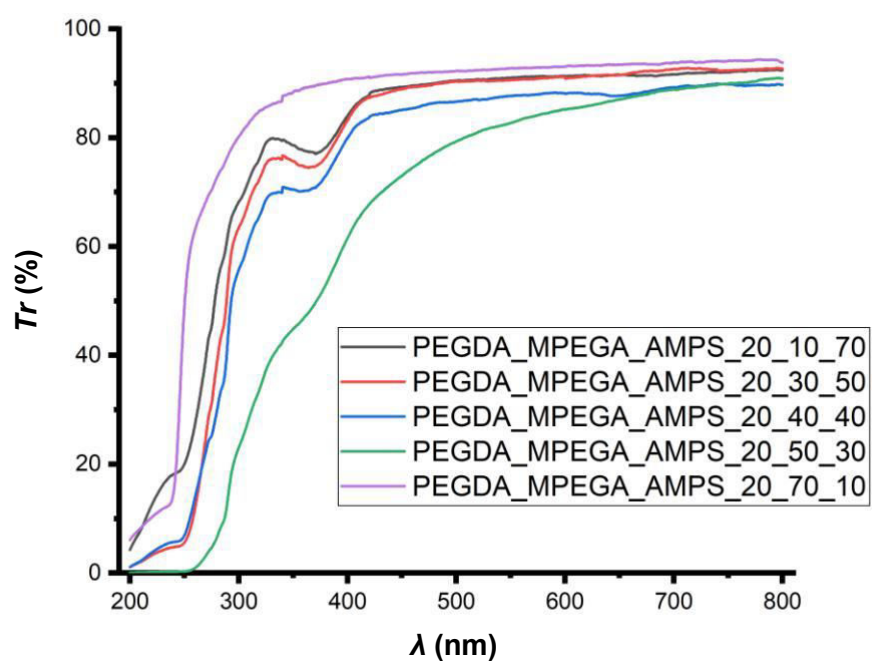


Figure F.68: Transmittance of 20% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

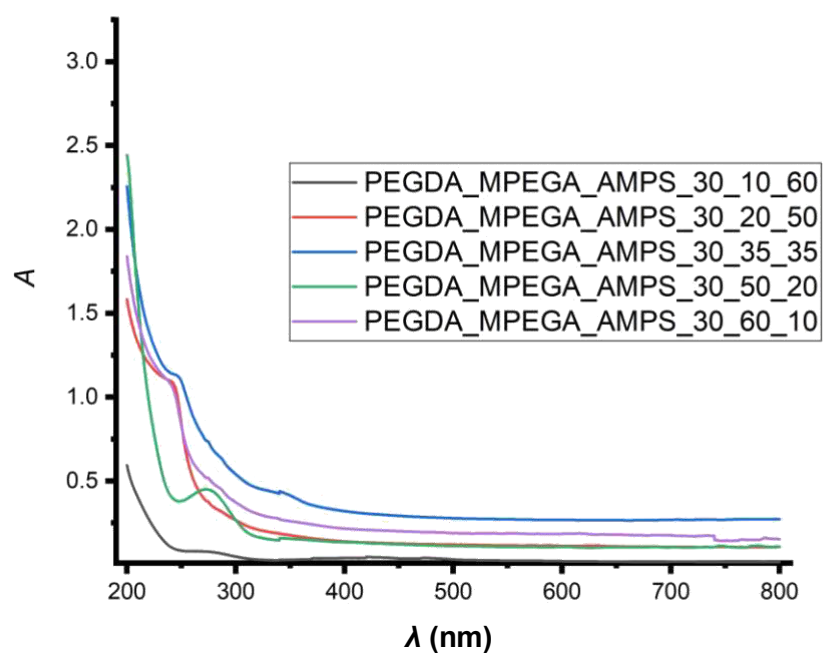


Figure F.69: Absorbance of 30% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

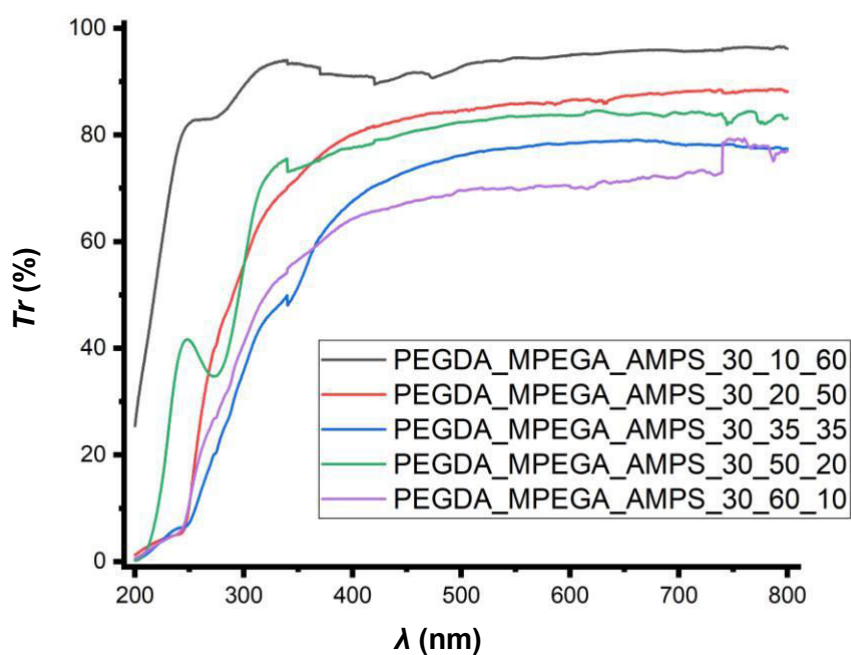


Figure F.70: Transmittance of 30% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

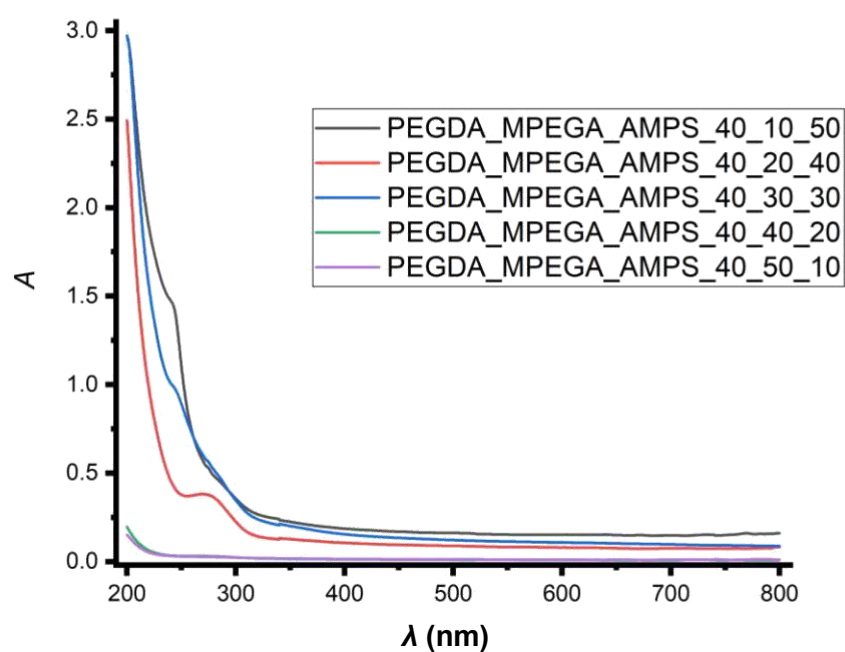


Figure F.71: Absorbance of 40% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

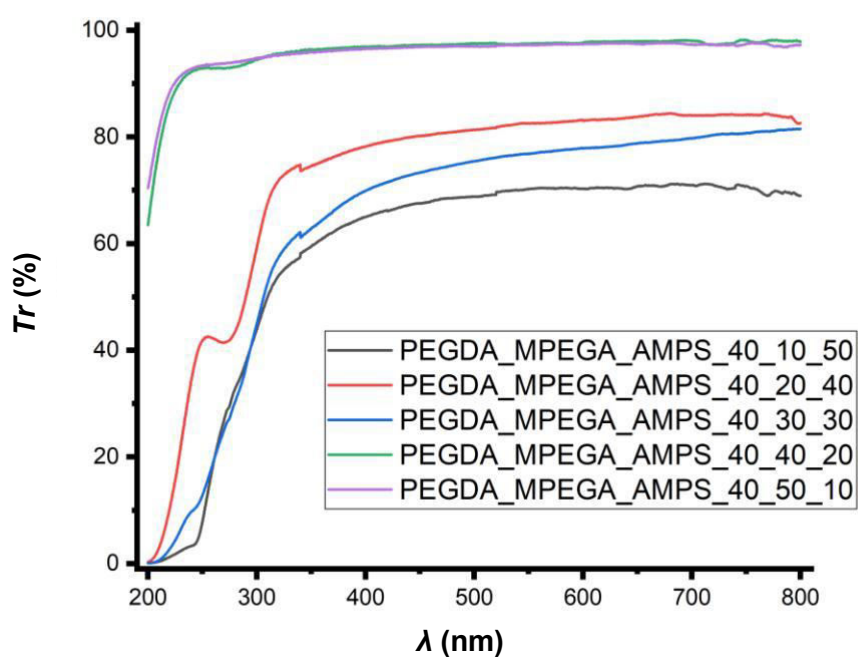


Figure F.72: Transmittance of 40% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

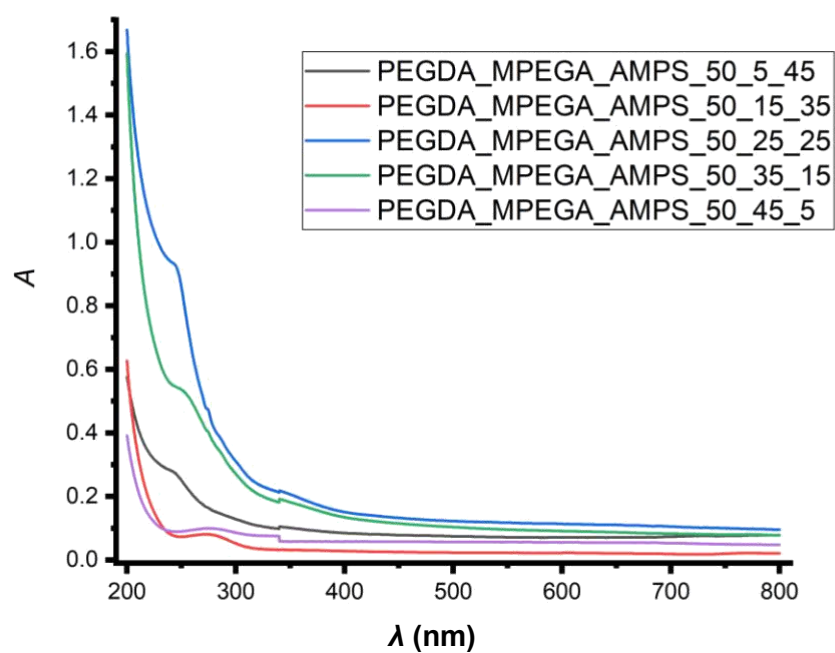


Figure F.73: Absorbance of 50% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

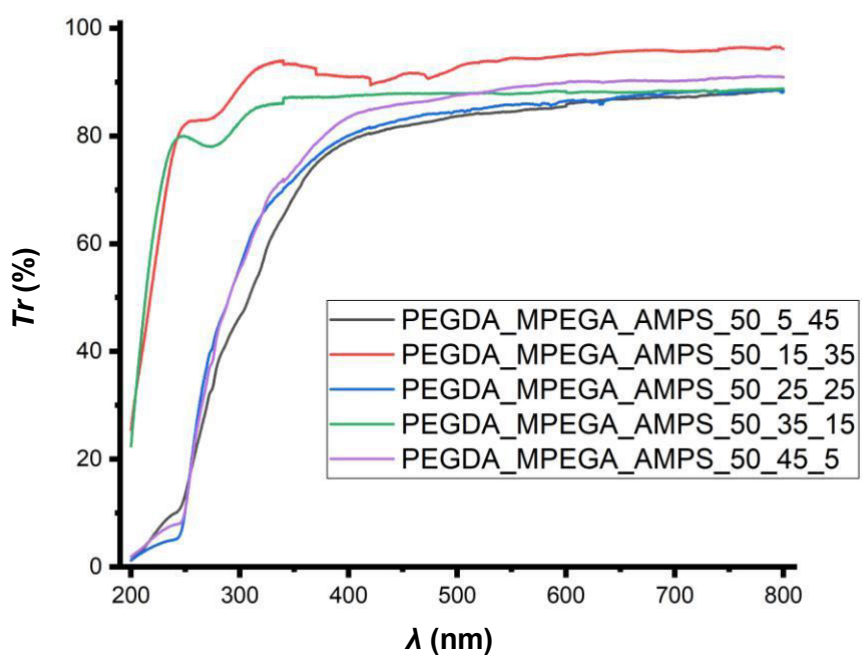


Figure F.74: Transmittance of 50% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

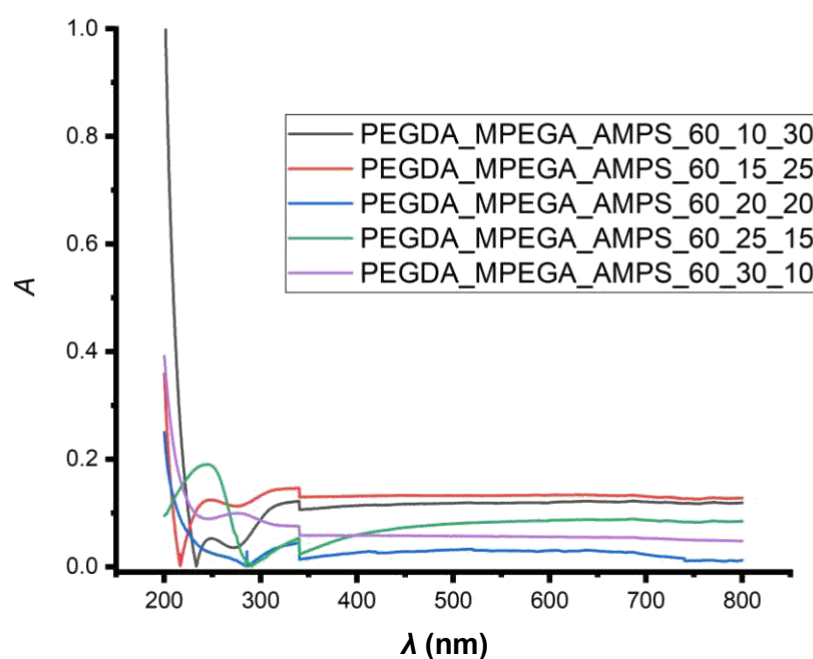


Figure F.75: Absorbance of 60% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

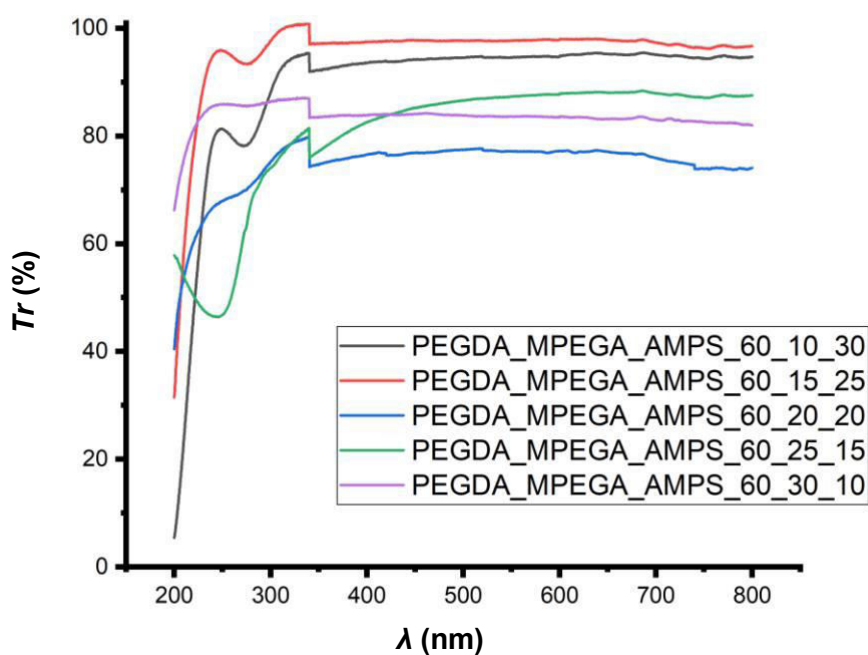


Figure F.76: Transmittance of 60% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

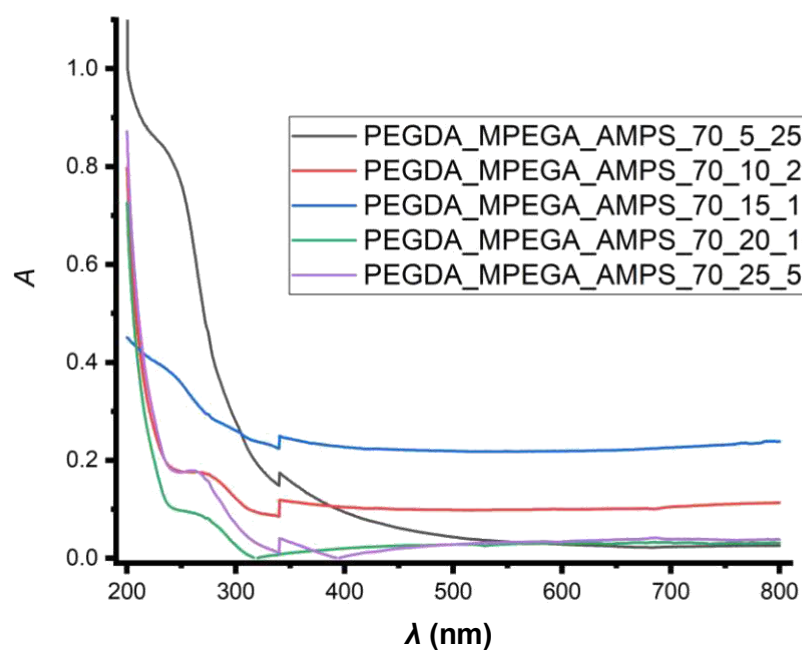


Figure F.77: Absorbance of 70% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

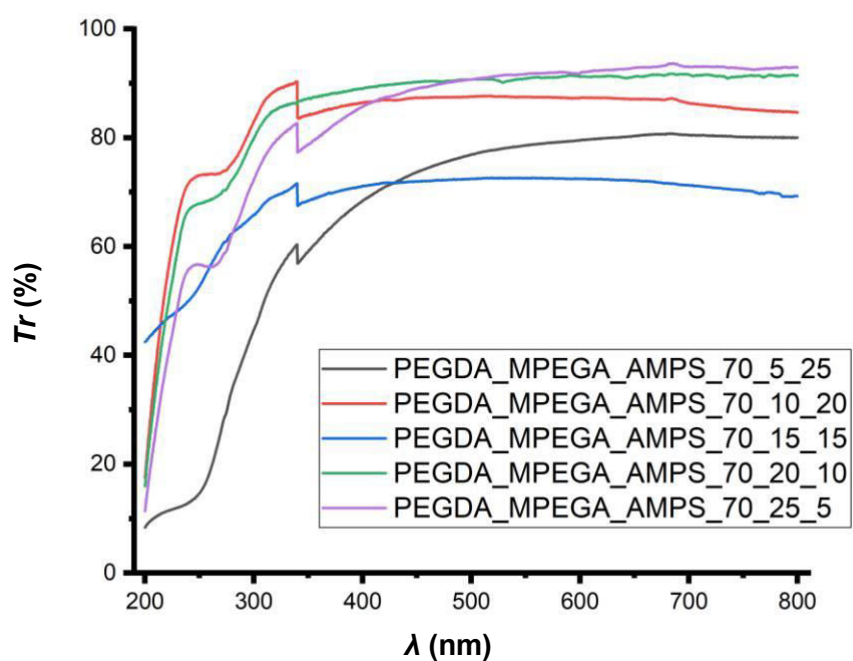


Figure F.78: Transmittance of 70% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

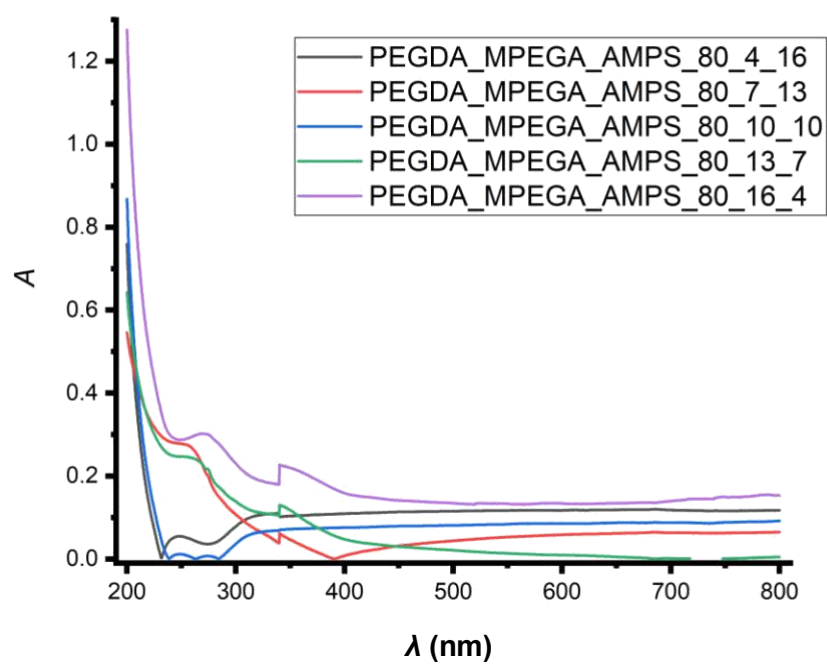


Figure F.79: Absorbance of 80% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

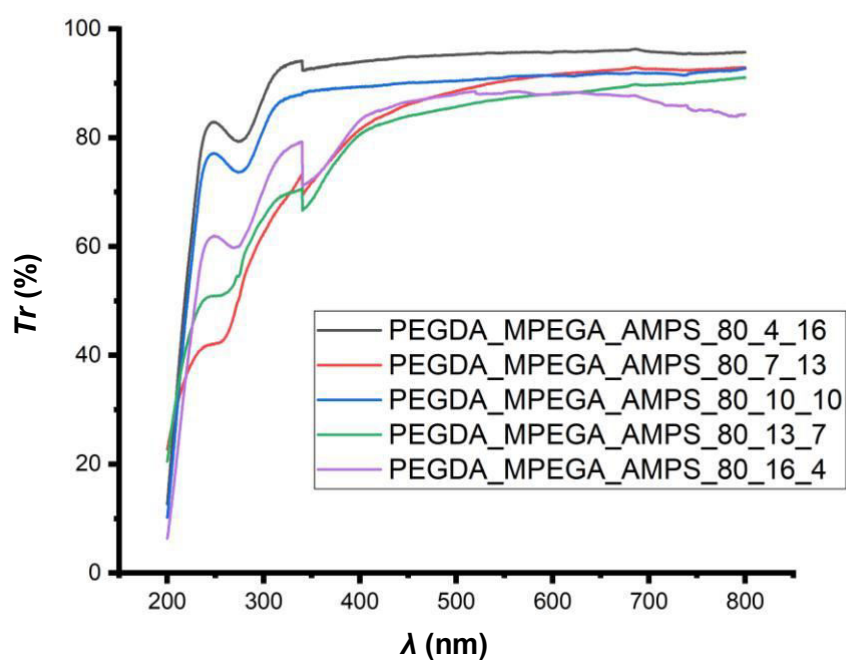


Figure F.80: Transmittance of 80% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

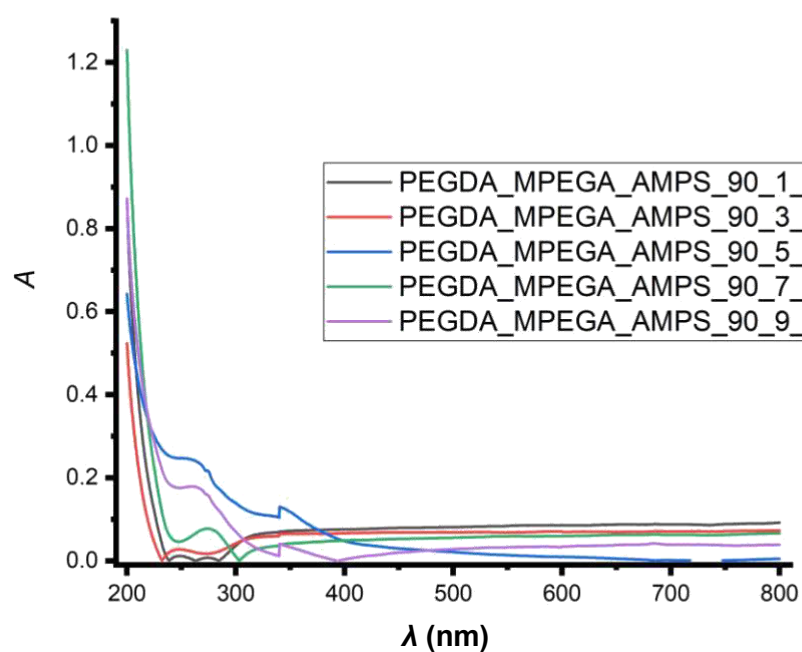


Figure F.81: Absorbance of 90% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength

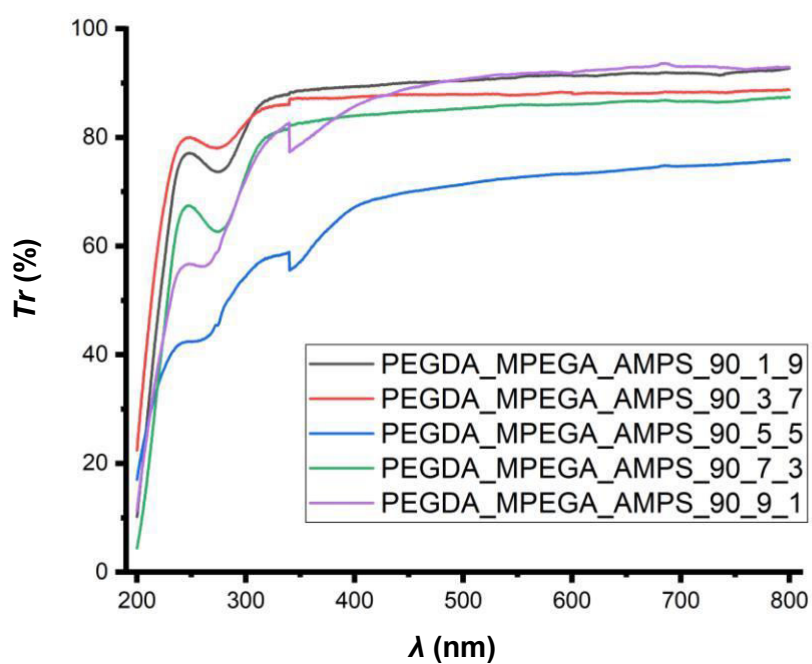


Figure F.82: Transmittance of 90% PEGDA-MPEGA-AMPS hydrogels as a function of wavelength