

Experimental report

16/08/2024

Proposal: 9-11-2140

Council: 4/2023

Title: Effect of the crosslinker nature (hyperbranched vs linear) on the structure of acrylic/silicone amphiphilic networks used for contact lenses

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Lionel PORCAR

Samples: C6H10O3 (HEMA acrylic monomer)
C3H8O3 (Hyperbranched polyglycerol cross-linker)
C17H38O6Si3 (SiGMA silicone monomer)
C33H86O12Si11 (butyl-PDMS silicone monomer)
C5H6O4 (itaconic acid to graft on the HPG cross-linker)
C6H9NO (NVP acrylic monomer)
C5H9O (DMA acrylic monomer)
C16H38O5Si4 (TRiS silicone monomer)
C14H22O6 (TEGDMA linear cross-linker)

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	0	2	07/09/2023 25/09/2023	08/09/2023 26/09/2023

Abstract:

Silicone contact lenses are composed of amphiphilic polymer `co-networks_c (APCN) mixing acrylic hydrogels with another (disconnected) silicone network. Silicone hydrogels show higher oxygen permeability than pure hydrogel contact lenses, due to the mobility and low cohesive energy of Si-O groups within the silicone backbone. However, the introduction of such silicone polymers reduces the hydrophilicity and hence the water content of the contact lenses, and also their wettability. The addition of hyperbranched polyglycerol (HPG) to the formulation of silicone hydrogel contact lenses may help to equilibrate the properties of oxygen permeability and water content, while also acting as a crosslinker. Thus it is necessary to establish the relationship between the structure of the hydrogel network at nanoscale and the oxygen permeability in order to know whether the silicone and hydrophilic domains will have a competitive or a synergic interaction.

Experimental Report

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Proposal number: 9-11-2140

Beamline: D22

Beamtime: 2 days (1+1), 23/09/7-8 and 23/09/25-26 (+ 23/09/20-21 at SOLEIL)

Date of report: 2024/08/14

- Objective & expected results:

Our objective was to study the nanostructure of industrially relevant contact lenses formulated with either hyperbranched polyglycerol or classical linear cross-linkers. Combining SANS at ILL and SAXS at SOLEIL gave us insight into the phase separation between the hydrophobic silicone domains and the hydrophilic chains (acrylic monomers and HPG cross-linker) and relate it to the O₂ permeability. A library of >100 contact lenses made of different silicone and hydrophilic monomers was synthesized and evaluated for their main properties (optical transparency, water retention...). The combined SANS-SAXS study enabled us rationalizing the structure-function relationship for these systems, evidencing the interest of the use of a hyperbranched polymer cross-linker such as HPG (potentially bio-sourced) patented by the French company Ophtalmic to decrease the silicone content in the contact lenses while keeping properties (light transparency, water equilibrium content, O₂ permeability and Young modulus).

- Results and the conclusions of the study:

Contact lenses are biomedical devices that correct ocular defects such as astigmatism, myopia, hypermetropia, and presbyopia. Based on their composition they can be classified as rigid, soft and hybrid.¹ Within soft contact lenses we can find silicone hydrogel contact lenses which are composed of amphiphilic polymer co-networks (APCN) mixing (meth)acrylic and vinylic polymer hydrogels with a silicone network.² Together they form an interpenetrated network (IPN) of silicone and hydrophilic chains.^{1,3,4} The main advantage of silicone hydrogels is that they show higher oxygen permeability than classical hydrogels due to the mobility and low cohesive energy of Si-O groups.⁵⁻⁸ In general, contact lenses should provide, good vision, comfort, and they should be able to allow an appropriate corneal metabolism. All these features depend on the optical (transparency, refractive index), chemical (water content and oxygen permeability),³ and mechanical (modulus)⁹ properties of the contact lenses. The goal of this investigation was to use a bifunctional hyperbranched polyglycerol (HPG-Al)¹⁰ as a crosslinker to obtain silicone hydrogel contact lenses. Contact lenses with different concentrations of crosslinkers and silicones were prepared by cast molding and characterized by a polarographic method, gravimetric analysis, and UV-vis spectroscopy to determine the oxygen permeability, equilibrium water content (EWC) and transparency (T%).

With the aim to study the structure-property relationship, a series of contact lenses (both dry and saturated with either 100% D₂O or 22:78 D₂O:H₂O mixture matching the hydrophilic components) were analyzed by SANS on D22 at the ILL and by SAXS and WAXS on SWING beamline at SOLEIL synchrotron.

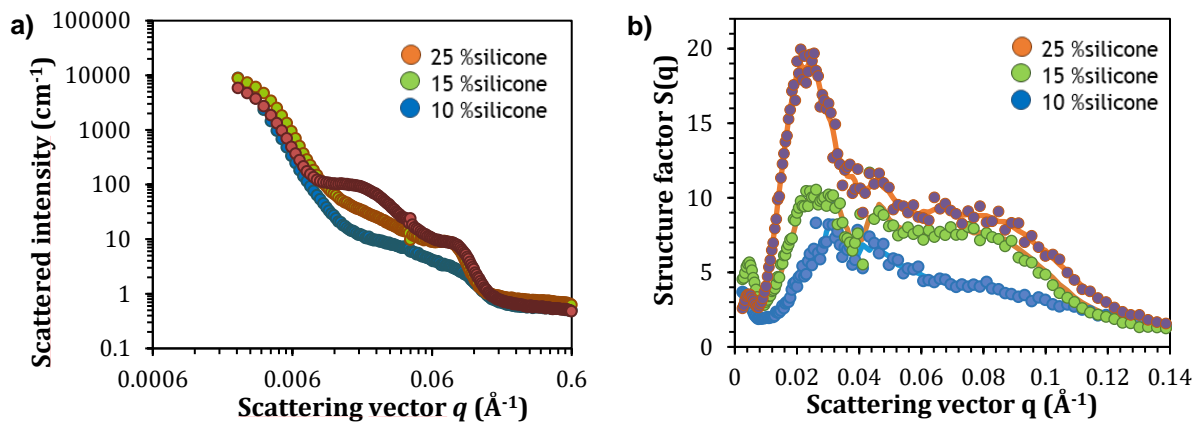


Figure 1. a) Small-angle neutron scattering curves for contact lenses with different silicone content (swollen in 100% D₂O); **b)** Structure factor obtained by dividing the intensity of the curves of the lenses in 100% D₂O by the intensity curves of the same contact lenses in the dry state.

The SANS, SAXS and WAXS curves were analyzed qualitatively and semi-quantitatively. For example, samples with identical monomers and crosslinkers yet varying silicone contents were compared in the swollen and dry states for the total contrast condition. We interpret the curves as typical of a composite of silicone domains embedded in the hydrophilic matrix. As shown on Fig. 1, we estimated the inter-particle structure factor, by analogy with silica-polymer composites in literature:¹¹ We found that $S(q)$ displays two peaks corresponding to domains at increasing mean distances with higher concentrations of silicone, in accordance with the decay of the oxygen permeability at higher silicone amounts. Additionally, swelling kinetics were carried out for selected contact lenses by following the time evolution of the scattering curve along hydration, from which water diffusion coefficients within the network were deduced (Fig. 2). Such measurements of swelling kinetics could be made only at ILL, with unique the controlled humidity cell available through partnership of soft condensed matter (PSCM), while SAXS measurements were done with special windows for gels.

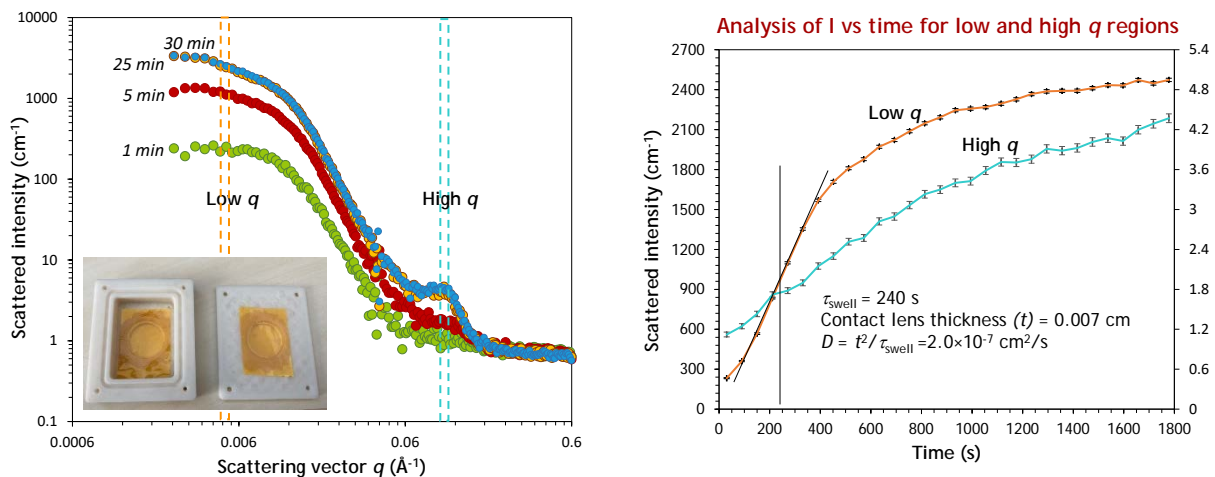


Figure 2. a) Kinetic study the SANS intensity increase from an initially dry lens (SLD contrast between acrylic and silicone chains) towards fully swollen lens (stronger SLD contrast between D₂O and all chains) thanks to the PSCM HR control cell; **b)** Characteristic time of gel swelling determined at low- q .

Our aim was also to measure other features such as the values of the two mesh sizes of the APCN structure for all the samples studied (~ 130 in total) and to correlate them with the macroscopic properties of the lens formulations (transparency, O₂ permeability and elastic modulus). The first analyses of SANS and SAXS/WAXS curves in terms of structure factor $S(q)$ enabled us showing that the characteristic distance ξ

between the network inhomogeneities increases with the silicone weight concentration, in agreement with the decrease of O₂ permeability. Further analysis of SAS data collection will consist in fitting curves of swollen contact lenses with gel models such as Teubner-Strey (double Lorentzian curves) or Debye-Bueche equations (inhomogeneities) to derive the mesh sizes of the two networks, respectively the hydrophilic acrylic network and the hydrophobic domains, which most likely consist into a array of isolated spheres rather than cylinders, as we initially imagined, explaining the limited O₂ permeability Dk of 50 barrer, at most.

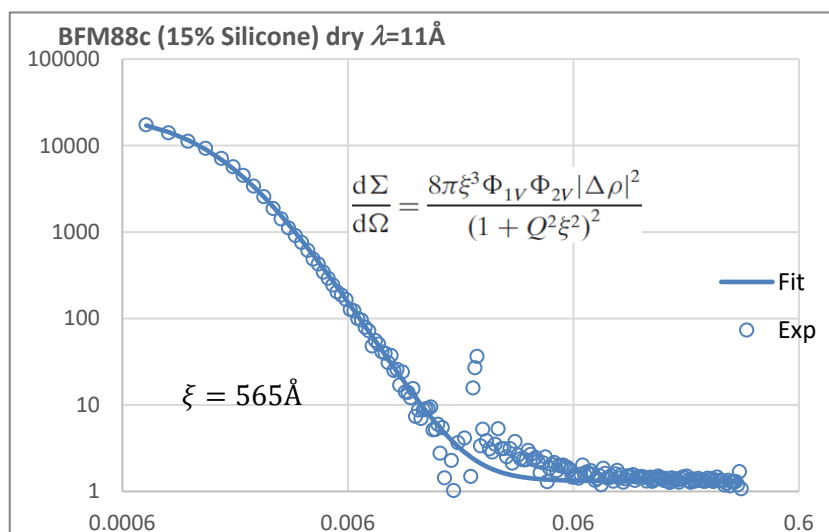


Figure 3. Fit of dry gel SAS curve with Debye-Bueche formula for inhomogeneities of mean size ξ

References:

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- 10 US20210369911A1, 2021, 1–18.
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- Justification and comments about the use of beam time:

We have gathered all the data we needed for our study, combining 2 runs of 8h at SOLEIL and 2 runs of 24h at ILL. 130 samples were measured in total, among which 53 at the ILL, both in the dry and the hydration states, with the kinetics for a few ones.

- Dissemination:

Several oral presentations were made on the study (51^{ème} Colloque du Groupe Français des Polymères (GFP2023), 20-24 Nov 2023, Bordeaux, France, 2nd French-Swiss Meeting “SANS for Soft Matter” – Paul Scherrer Institute, Villigen, Switzerland, Jan 24-25, 2024, [2FDN “Workshop Neutrons & Health”](#), Paris, 19-20 Mar 2024. Publication in preparation, to be submitted in *Macromolecular Rapid Communications*.