Synthesis of amphiphilic co-networks based on PEG and PCL 4-armed star polymers with model character

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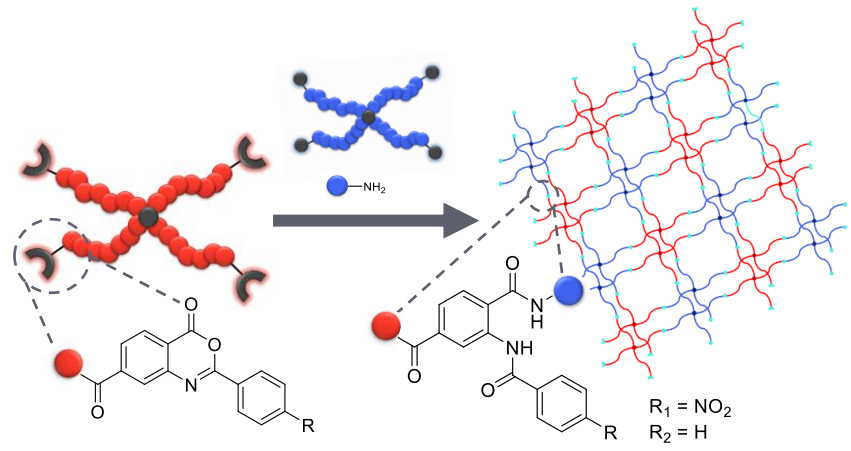
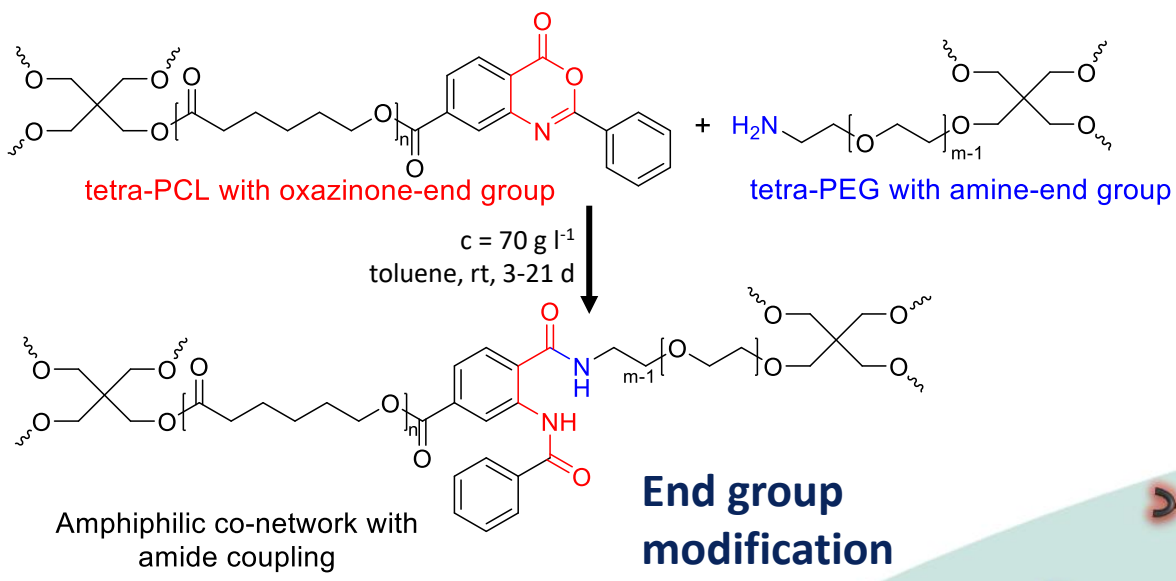
Introduction

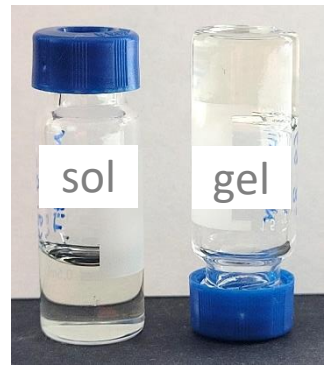
Controlled synthesis of model amphiphilic co-networks (ACNs) is based on the hetero-complementary linkage of 4-arm polymer stars with a defined length and number of monodisperse polymer strands. Previous studies on hydrophilic polyethylene glycol stars (tetra-PEG/tetra-PEG)[1] and the synthesis and characterization of hydrophobic ε-polycaprolactone- with tetra-PEG stars (tetra-PCL/tetra-PEG-1, R = NO_2)[2] provided valuable insights into crosslinking strategies. NMR spectroscopic studies of our new system (R = H) show a clear influence of the end group on the kinetics of network formation, as well as the nature of the linkage.



Synthesis Strategy

The synthesis of the ACNs including tetra-PCL with an oxazinone end group (tetra-PCL-Ox, R = H) and tetra-PEG with an amino end group (tetra-PEG-NH_2) was carried out using stock solutions of the 4-arm stars at a concentration of 70 g l^{-1}. These stock solutions were mixed, and the reaction was carried out at room temperature (rt).





Characterization

Various investigations were carried out to characterize the ACNs. NMR spectroscopy was used to determine the reaction kinetics of network formation and the degree of cross-linking. In addition, the degree of equilibrium swelling was determined.

NMR Spectroscopy

Investigation of the time-dependent gelation kinetics of the cross-linking reaction between tetra-PCL-Ox and tetra-PEG-NH_2. *In situ* ^{1}H NMR measurements of the reacting mixture at 30 °C in toluene-d_8 at a concentration of 70 g l^{-1} show the formation of an amide bond over 24 hours. In comparison to Bunk *et al.*[2] (R = NO_2), where a binding signal was detected after 3 minutes, our system (R = H) showed an amide binding signal after 20 minutes.

MQ NMR Spectroscopy

A comparison of the different connectivity fractions obtained for the various networks is presented. PEG-PEG was synthesized in D_2O according to the method of Sakai *et al.*[1]. PCL-PEG-1 (R = NO_2) was synthesized in toluene-d_8 according to the method of Bunk *et al.*[2]. PCL-PEG-2 (R = H) was synthesized in toluene-d_8 according to our new method.

Equilibrium Swelling Experiment

Illustration of the network synthesis time using the equilibrium degree of swelling (Q_v) of the ACNs synthesized in toluene. A comparison of the network synthesis times for 3, 7 and 21 days is shown. The first column shows Q_{v1} of the preparation state. The following three columns show the consecutive swelling-drying cycles (Q_{v2}–Q_{v4}).

Summary and Outlook

Initial results of the present study show that the ACN synthesis of the tetra-PCL-Ox (R = H) and tetra-PEG-NH_2 system exhibits slower kinetics than the tetra-PCL-Ox-NO_2 system in previous work.[2] Using equilibrium swelling degrees, it was possible to determine that the system requires a reaction time of at least 21 days to reach the equilibrium. ACNs with hetero-complementary coupling involving a carb-oxylic acid end group and an amino end group, as well as an imidazole end group and a bromine end group, also show promising results.

References

[1] Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U. I., *Macromolecules* **2008**, *41*, 5379.

[2] Bunk, C.; Löser, L.; Fribiczer, N.; Komber, H.; Jakisch, L.; Scholz, R.; Voit, B.; Seiffert, S.; Saalwächter, K.; Lang, M.; Böhme, F., *Macromolecules* **2022**, *55*, 6573.