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Toward Sustainable Alternatives: Isocyanate-Free Hydrophobically Modified Ethoxylated Urethanes

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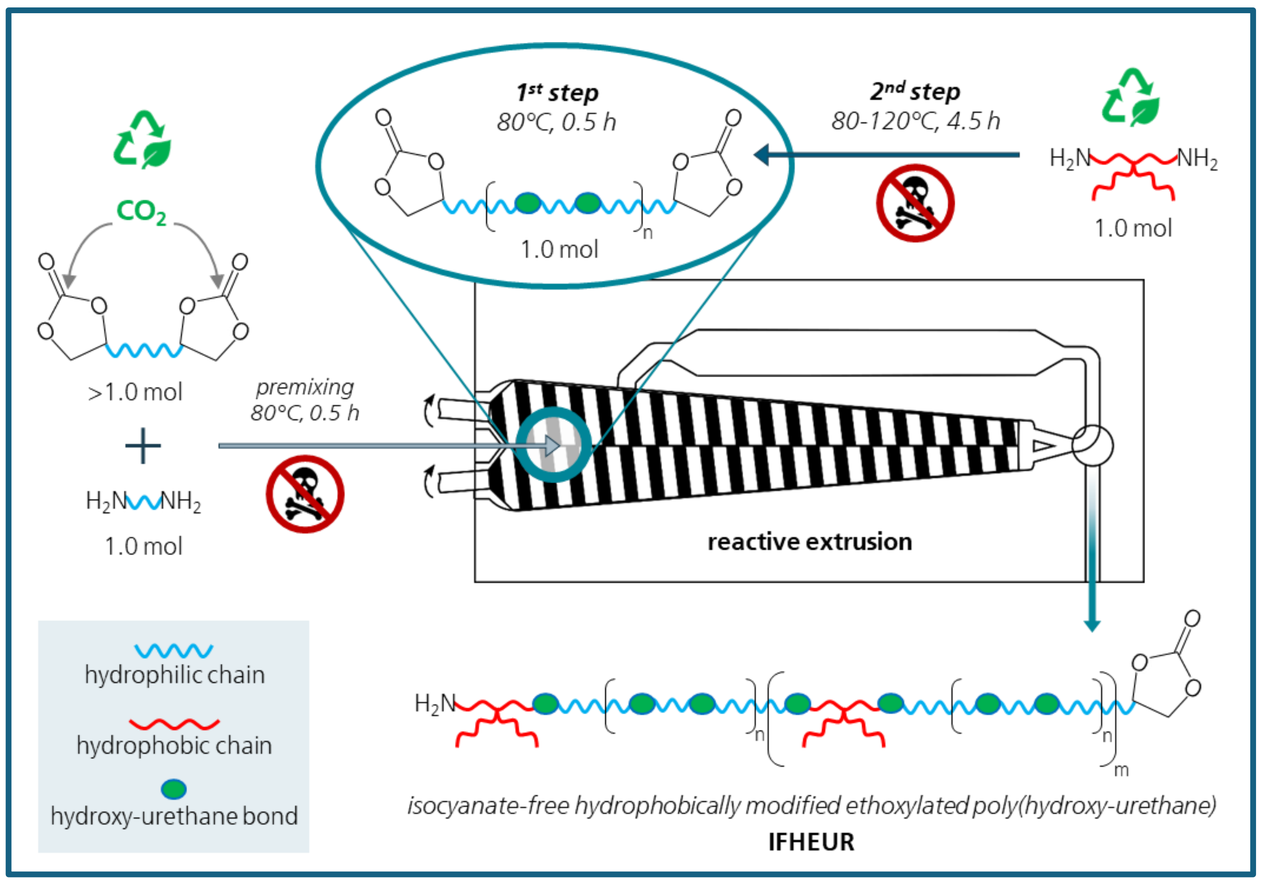
Introduction: Hydrophobically modified ethoxylated urethanes (HEURs) are common in **paints and coatings**, where they boost viscosity through **micelle** formation. However, their production involves **toxic isocyanates**, raising health and environmental concerns. In our work, we developed a greener alternative - **isocyanate-free HEURs (IFHEURs) -** by using **carbon dioxide** and **bio-based** building blocks. These new polymers not only avoid harmful chemicals but also incorporate CO_2 during synthesis, improving sustainability.

The goal of the study: Our aim was to design and test new rheology modifiers made from IFHEURs using a **safer, more sustainable** method. We tackled the slow reactivity of 5-membered poly(etylene glycol) bis(cyclic carbonate) with a hydrophilic diamine (4,7,10-trioxa-1,13-tridecanediamine) by applying **reactive extrusion (REX)**, an efficient, **solvent-free** technique. This allowed us to link a CO_2-based hydrophilic prepolymer with a renewable, hydrophobic fatty diamine (PRIAMINE 1075).



Green synthesis approach for IFHEUR rheology modifiers containing pendant and terminal hydrophobic groups

Results: Spectroscopic methods (NMR, FT-MIR) and SEC confirmed the unique structure of IFHEURs with both terminal and internal hydrophobic moities. Rheological tests showed that these polymers form strong, network-like associations in water, providing excellent thickening even at low concentrations.

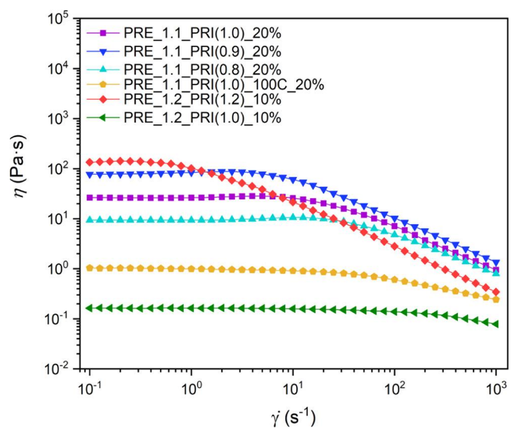


Figure 1. *Plots of steady shear viscosity (η) in dependence of shear rate (γ) for the aqueous solutions of IFHEUR at indicated concentration.*

Rheological studies for IFHEUR 10 and/or 20 wt% aqueous solutions:

Left: Steady-shear behavior

Bottom: Oscillatory shear measurements

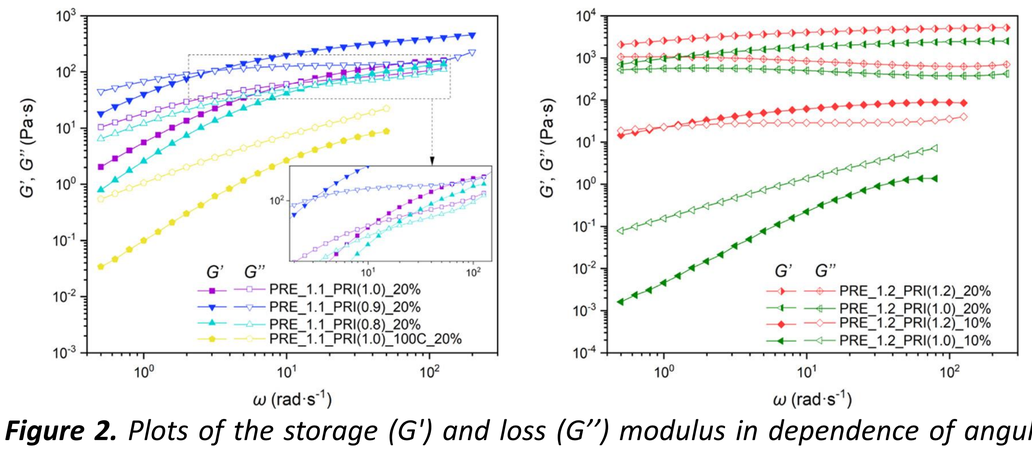


Figure 2. *Plots of the storage (G') and loss (G'') modulus in dependence of angular frequency (ω) for the aqueous solutions of IFHEUR.*

Table 1. *Prepared formulation of IFHEURs along with the results of NMR and SEC measurements.*

Samples	Urethane groups [mol%]	Carbonate groups [mol%]	Amine groups [mol%]	M_w [g·mol^{-1}]	Dispersity [-]
PRE_1.1_PRI(0.8-1.0)	22.5 - 24.2	1.8 - 4.0	1.0 - 1.7	36 500 – 46 300	2.7 - 4.7
PRE_1.2_PRI(1.0-1.2)	25.3 - 25.9	0.5 - 1.0	1.2 - 2.1	23 900 - 39 700	2.5 - 3.4

Conclusions:

- An innovative concept to prepare an **eco-friendly alternative** to **HEUR**-based associative thickeners was revealed.
- The toxic reactants were replaced with **green chemicals and efficient, solvent-free REX** was applied to obtain **CO_2-based IFHEURs**.
- The structure of **IFHEURs** differing in molecular architecture was proved by means of **NMR** and **FT-MIR** spectroscopies, as well as **SEC**.
- The unique architecture of the obtained **IFHEURs**, containing **both terminal and inner hydrophobic groups**, had a crucial impact on their rheological performance in aqueous solutions.
- Both steady shear and oscillatory measurements confirmed that the **IFHEUR** molecules with sufficient chain length associate into mechanically active intermicellar crosslinks.
- With growing access to commercial cyclic carbonate monomers, the **isocyanate-free synthesis pathway** toward **IFHEURs** offers tremendous potential to deliver **sustainable rheological modifiers for waterborne systems**.

Bibliography:
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