Influence of the polymer matrix on the viscoelastic behaviour of vitrimers

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Thermal and IR Characterization

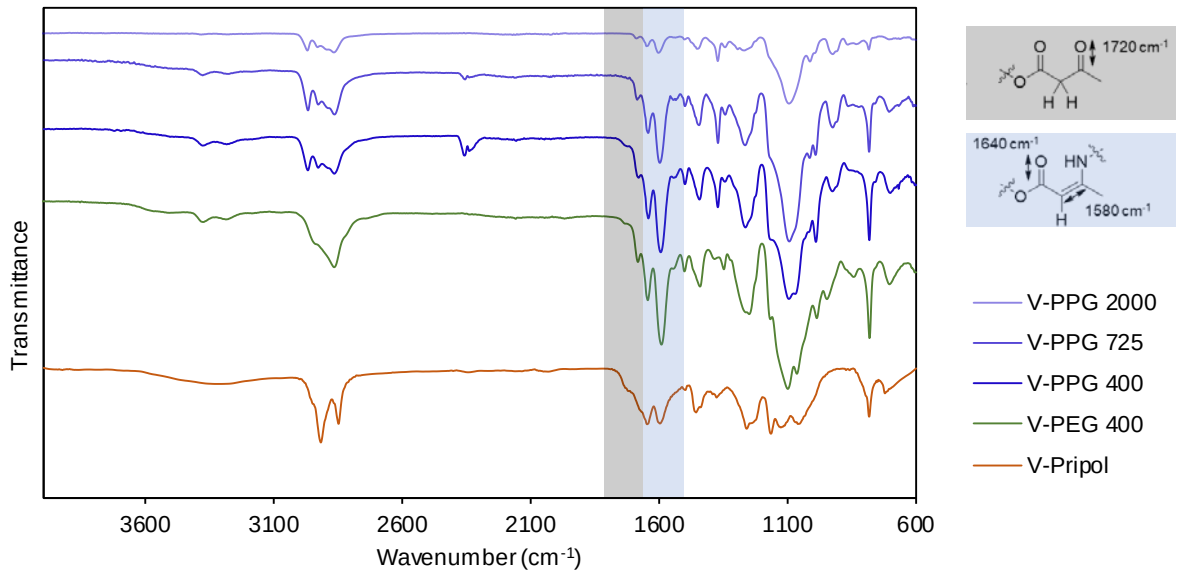

Figure S 1. ATR-FTIR spectra of polypropylene glycol (V-PPG: top to bottom 2000, 725, 400 g.mol^{-1}), polyethylene glycol (V-PEG: 400 g.mol^{-1}) and pripol (V-Pripol) based vinylogous urethane networks.

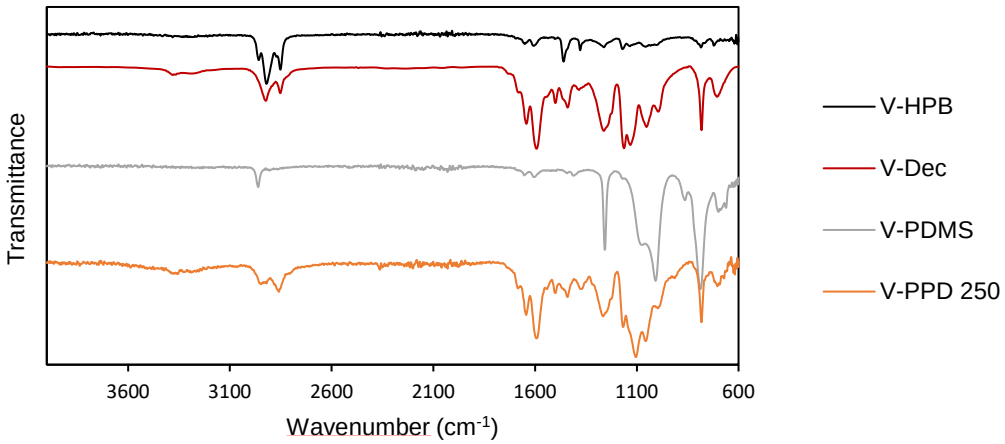

Figure S 2. ATR-FTIR spectra of hydrogenated polybutadiene (V-HPB) (HPB, 3100 g.mol^{-1}; V-HPB), 1,10-Decanediol (V-Dec), PDMS (V-PDMS) (5600 g.mol^{-1}) and polypropanediol (V-PPD) (PPD, 250 g.mol^{-1}) based vinylogous urethane networks.

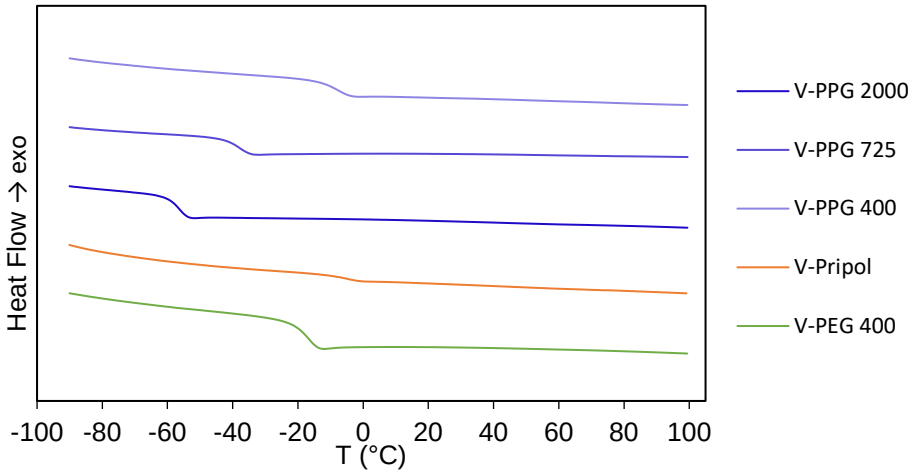

Figure S 3. Differential scanning calorimetry thermograms of vitrimers based on PPG with different molecular weights (400, 725 and 2000 g.mol^{-1}), Pripol, and PEG (400 g.mol^{-1}) with a heating and cooling rate of 10 K.min^{-1}.

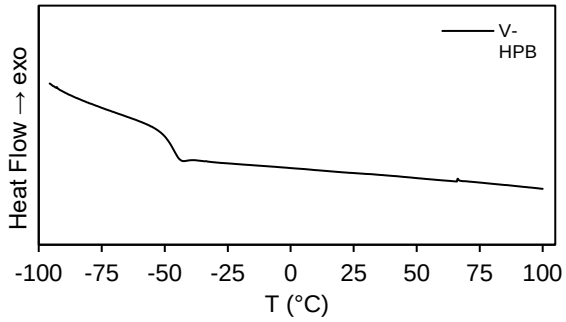

Figure S 4. DSC thermogram of HPB-based vitrimer with a heating and cooling rate of 10 K.min^{-1}.

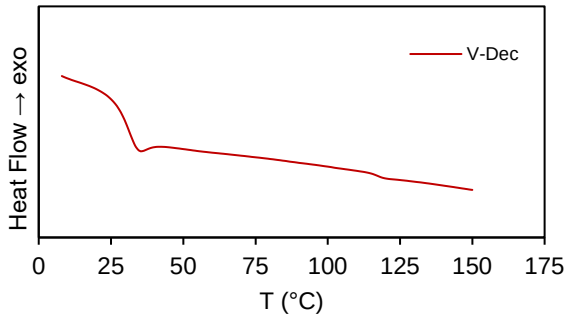

Figure S 5. DSC thermogram of 1,10-Decanediol-based (V-Dec) vitrimer with a heating and cooling rate of 10 K.min^{-1}.

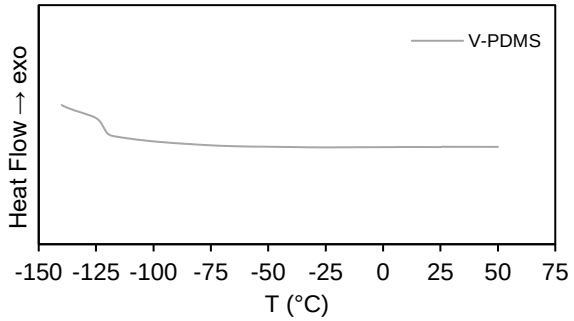

Figure S 6. DSC thermogram of PDMS-based vitrimer with a heating and cooling rate of 10 K.min^{-1}.

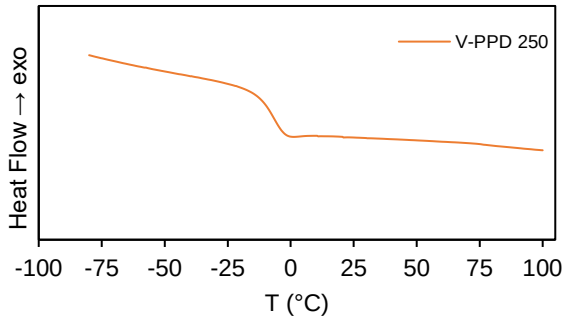

Figure S 7. DSC thermogram of PPD_{250} based vitrimer with a heating and cooling rate of 10 $K.min^{-1}$.

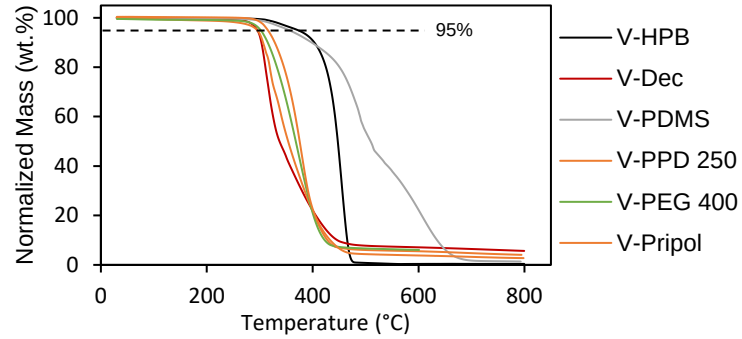

Figure S 8. TGA measurements of the HPB, Dec, PDMS, PPD_{250}, PEG_{400} and pripol-based vitrimers with a temperature ramp from 25 to 800 °C at 10 $K.min^{-1}$ under N_2 atmosphere.

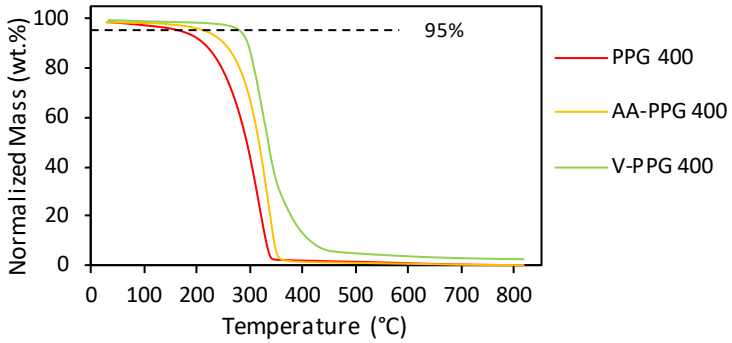

Figure S 9. TGA measurements of PPG_{400} diol, acetoacetylated PPG_{400} (AA-PPG 400) and V-PPG_{400} with a temperature ramp from 25 to 800 °C at 10 $K.min^{-1}$ under N_2 atmosphere.

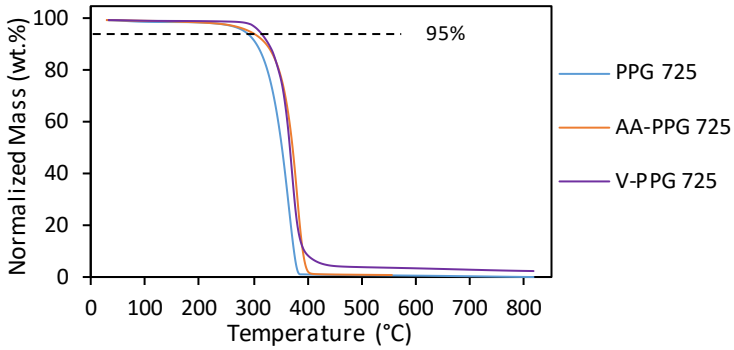

Figure S 10. TGA measurements of PPG_{725} diol, acetoacetylated PPG_{725} (AA-PPG 725) and V-PPG_{725} with a temperature ramp from 25 to 800 °C at 10 $K.min^{-1}$ under N_2 atmosphere.

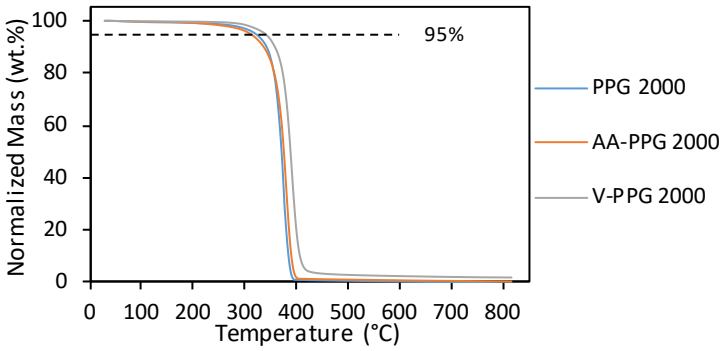

Figure S 11. TGA measurements of PPG_{2000} diol, acetoacetylated PPG_{2000} (AA-PPG 2000) and V-PPG_{2000} with a temperature ramp from 25 to 800 °C at 10 K.min^{-1} under N_2 atmosphere.

Rheological characterization

Time Sweep

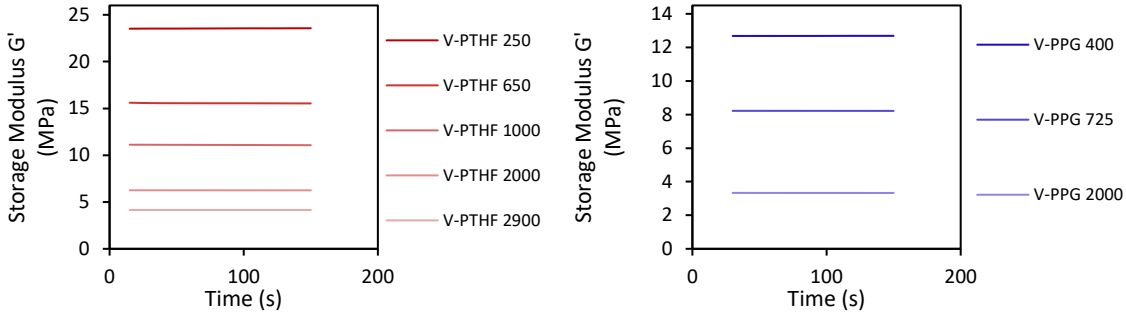

Figure S 12. Time sweep experiments of the different PTHF and PPG-based vitrimers at 150 °C, showing the storage modulus as a function of time.

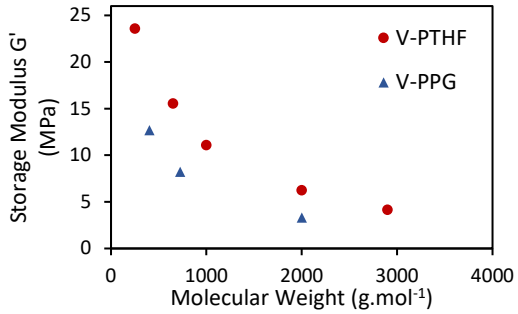

Figure S 13. Storage modulus (obtained via *time sweep experiments at 150 °C) of the PTHF and PPG-based vitrimers as a function of the molecular weight of the macromonomer.*

Stress relaxation and Arrhenius plots

1) Polyethers
    a. PTHF-based vitrimers

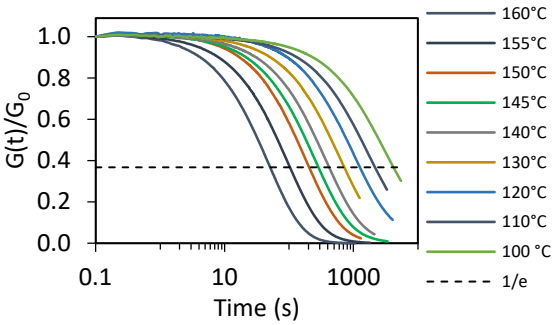

Figure S 14. Stress relaxation experiments at different temperatures for V-PTHF$_{250}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

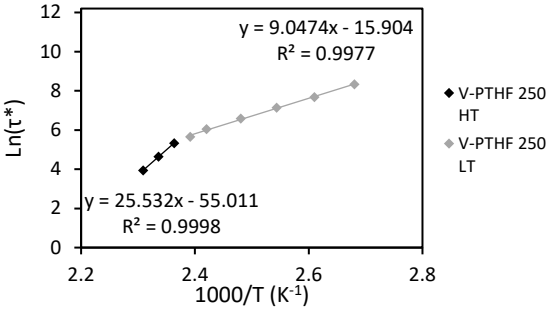

Figure S 15. Arrhenius plot for V-PTHF$_{250}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

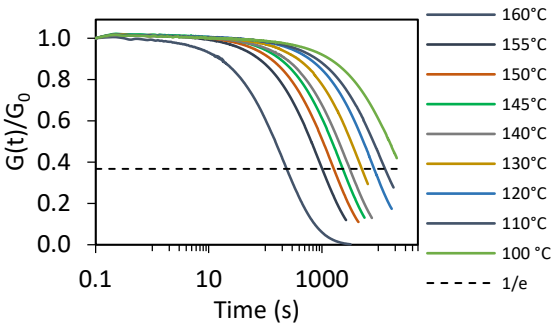

Figure S 16. Stress relaxation experiments at different temperatures for V-PTHF$_{650}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

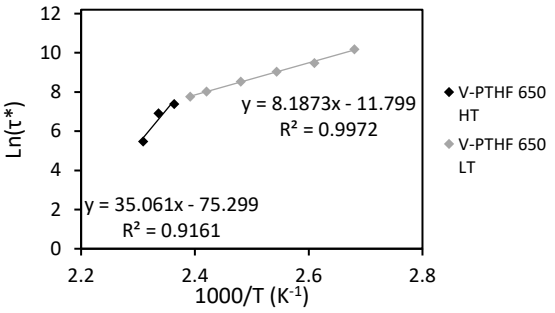

Figure S 17. Arrhenius plot for V-PTHF$_{650}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

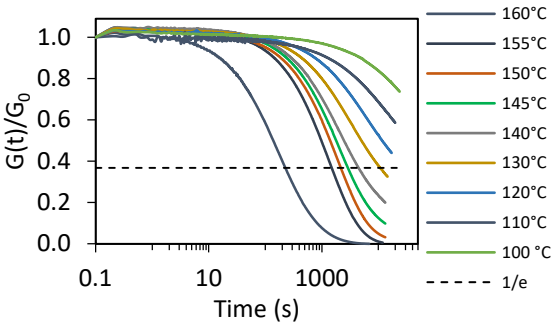

Figure S 18. Stress relaxation experiments at different temperatures for V-PTHF$_{1000}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

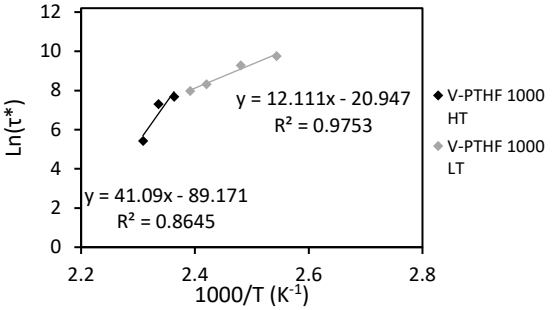

Figure S 19. Arrhenius plot for V-PTHF$_{1000}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

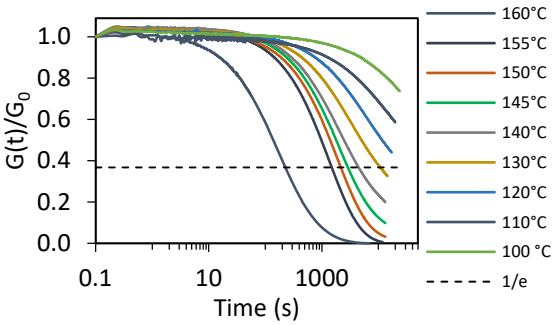

Figure S 20. Stress relaxation experiments at different temperatures for V-PTHF$_{2000}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

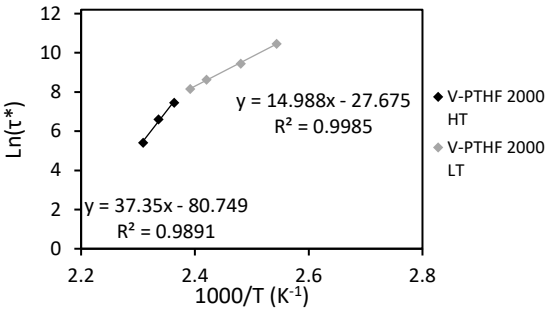

Figure S 21. Arrhenius plot for V-PTHF$_{2000}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

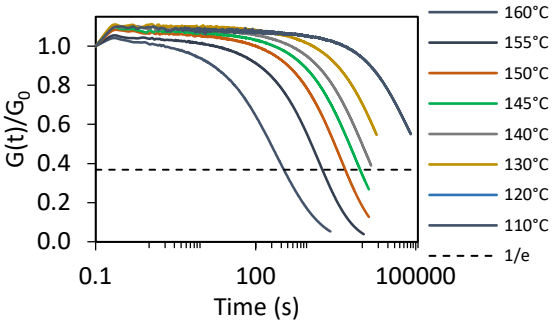

Figure S 22. Stress relaxation experiments at different temperatures for V-PTHF$_{2900}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

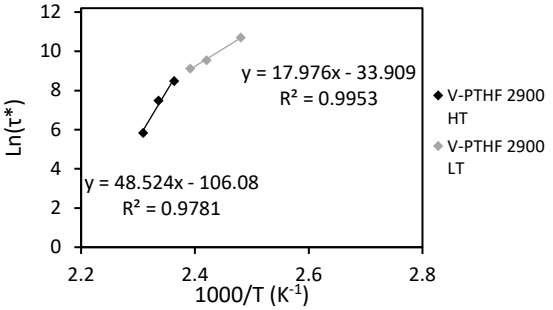

Figure S 23. Arrhenius plot for V-PTHF$_{2900}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

b. PPG-based vitrimers

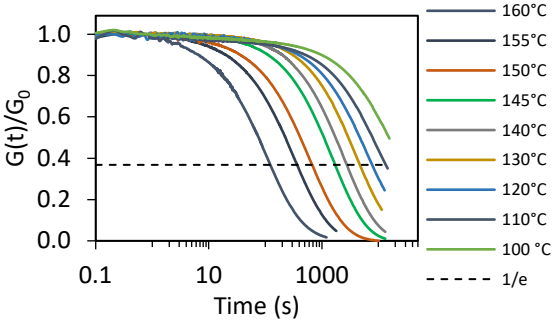

Figure S 24. Stress relaxation experiments at different temperatures for V-PPG$_{400}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

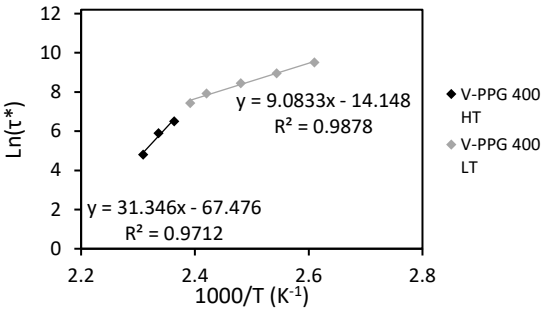

Figure S 25. Arrhenius plot for V-PPG$_{400}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

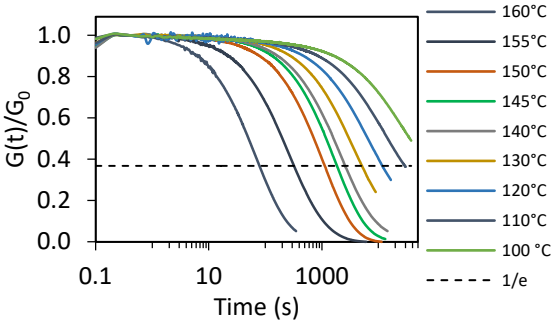

Figure S 26. Stress relaxation experiments at different temperatures for V-PPG$_{725}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

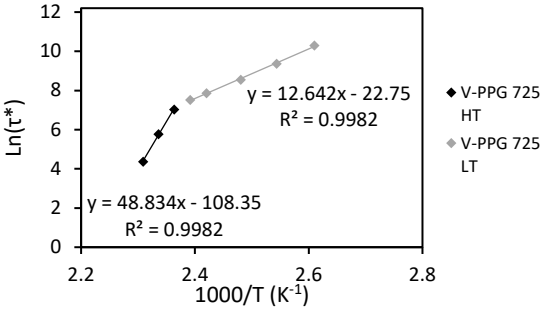

Figure S 27. Arrhenius plot for V-PPG$_{725}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

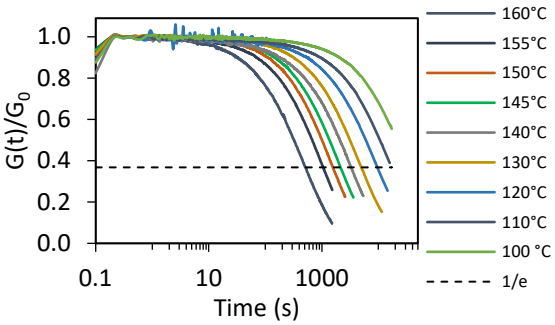

Figure S 28. Stress relaxation experiments at different temperatures for V-PPG$_{2000}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

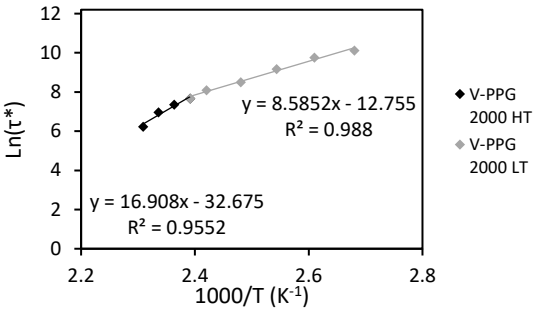

Figure S 29. Arrhenius plot for V-PPG$_{2000}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

c. PEG-based vitrimer

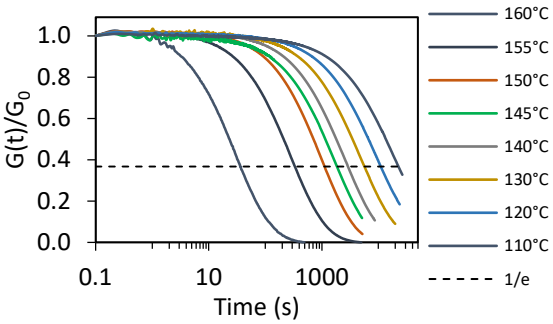

Figure S 30. Stress relaxation experiments at different temperatures for V-PEG$_{400}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

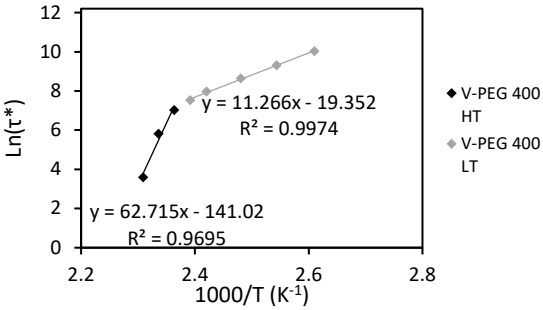

Figure S 31. Arrhenius plot for V-PEG$_{400}$, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

d. PPD-based vitrimer

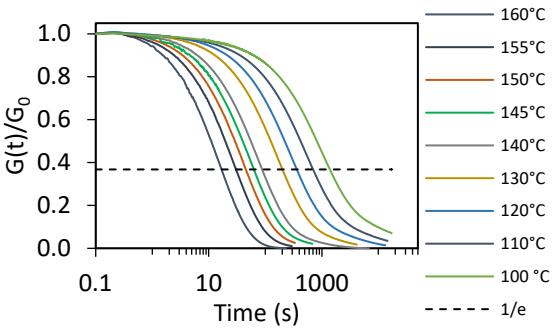

Figure S 32. Stress relaxation experiments at different temperatures for V-PPD$_{250}$. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

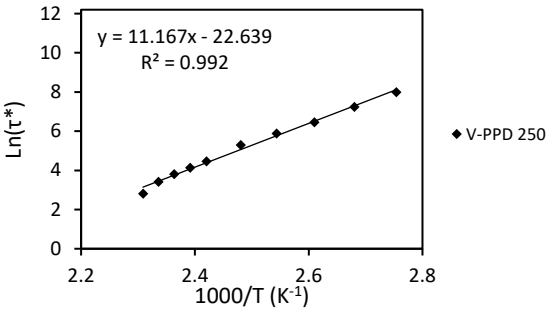

Figure S 33. Arrhenius plot for V-PPD$_{250,}$ showing only one temperature dependency region, used for the calculation of the activation energies.

2) Others

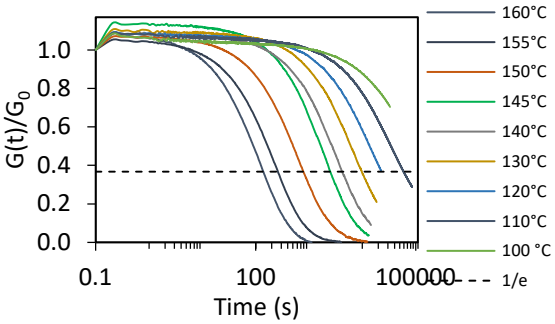

Figure S 34. Stress relaxation experiments at different temperatures for V-HPB. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

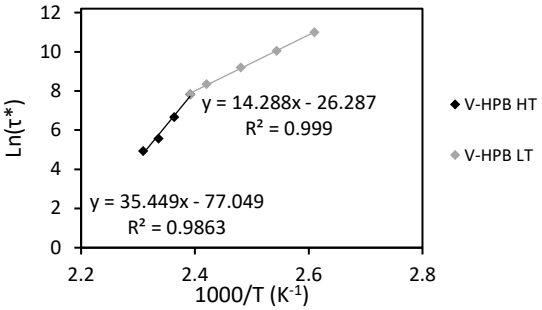

Figure S 35. Arrhenius plot for V-HPB, showing the high temperature (HT) and low temperature (LT) region, used for the calculation of the activation energies.

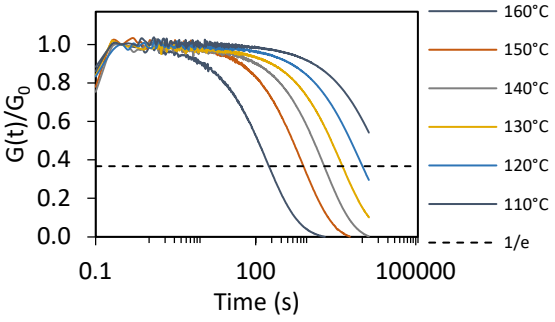

Figure S 36. Stress relaxation experiments at different temperatures for V-PDMS. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

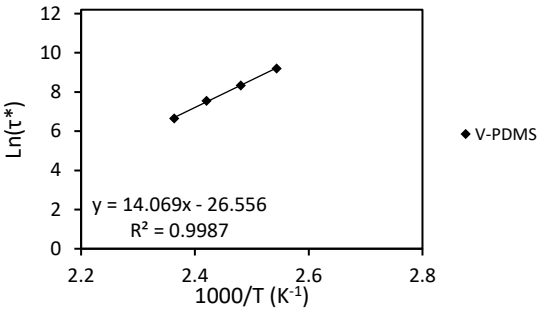

Figure S 37. Arrhenius plot for V-PDMS, showing only one temperature dependency region, used for the calculation of the activation energies.

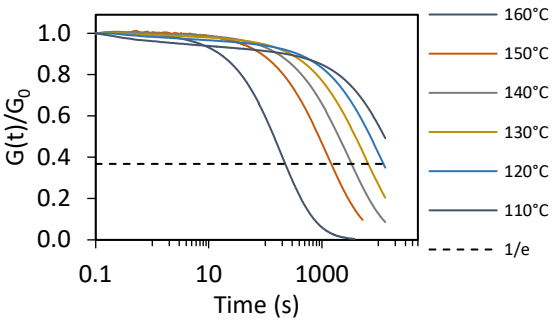

Figure S 38. Stress relaxation experiments at different temperatures for V-Dec. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

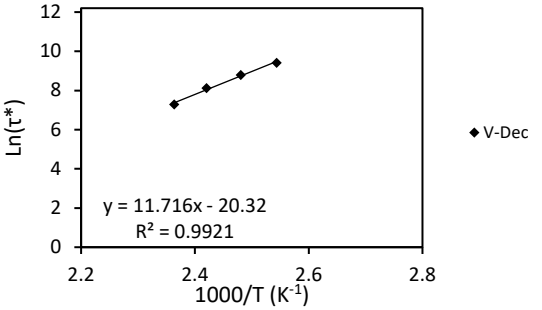

Figure S 39. Arrhenius plot for V-Dec, showing only one temperature dependency region, used for the calculation of the activation energies.

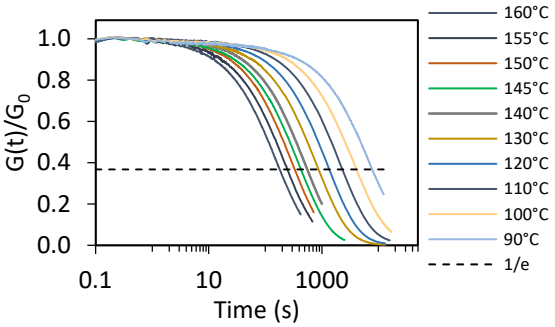

Figure S 40. Stress relaxation experiments at different temperatures for V-Pripol. The black dotted line represents $G(t)/G_0 = 1/e$, which defines the characteristic relaxation time τ^*.

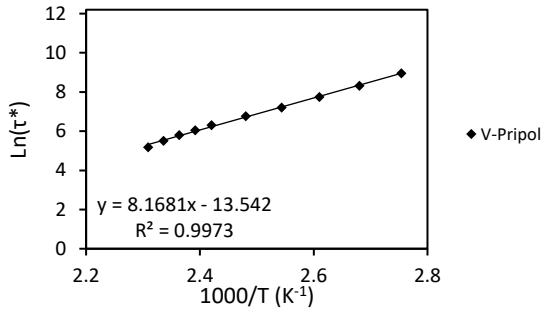

Figure S 41. Arrhenius plot for V-Pripol, showing only one temperature dependency region, used for the calculation of the activation energies.

Solvatation effect

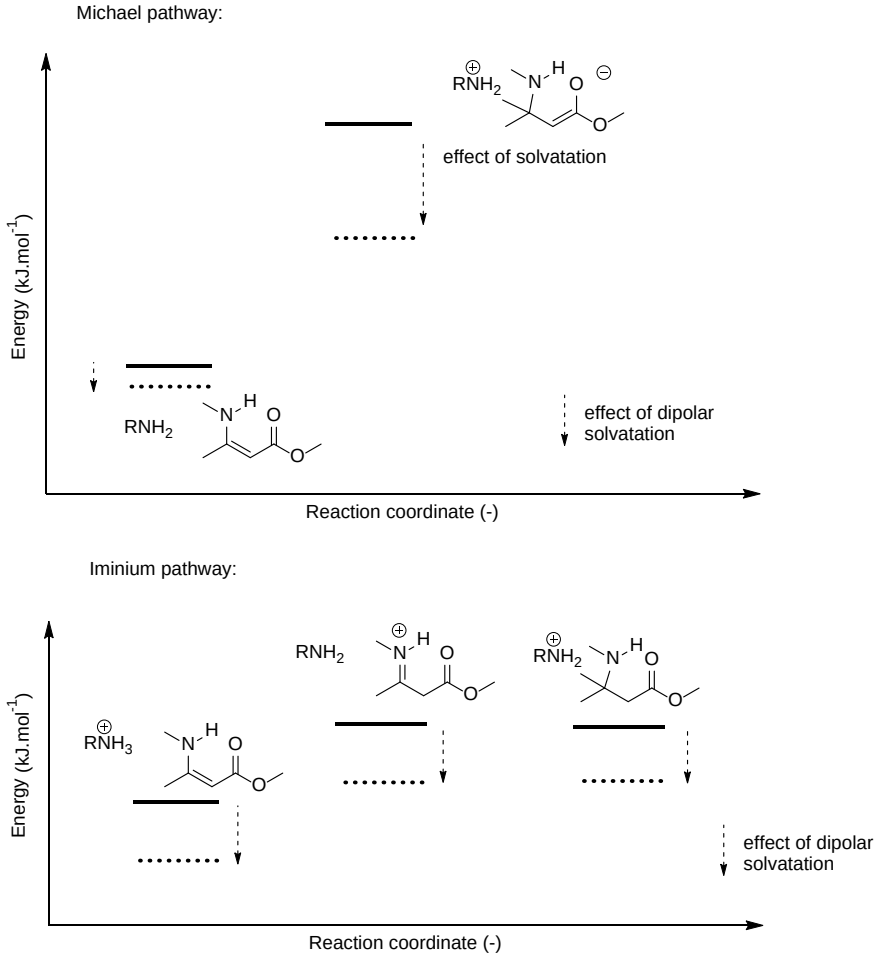

Figure S 42. Schematic representation of a dipolar solvatation effect on the Michael and Iminium pathway.

Literature and commercial values

Table S1 Solubility parameters and dielectric constants of the investigated diols and the activation energy of their corresponding vitrimers.

Diol	Solubility parameter $(MPa)^{1/2}$	Dielectric constant ε_r	E_a (I) $(kJ.mol^{-1})$
PDMS	15.3[a]	2.3-2.5[b]	117
HPB	16.7[d]	n/a	119
PPG	17.2[a]	2.5[a]	71-105
Decanediol	17.5[b]	8.1[c]	97
pTHF	17.5[a]	2.5[a]	68-149
PPD	19.2[a]	n/a	93
PEG_{400}	20.8[a]	12.4[e]	94
Pripol	n/a	n/a	68

[a] Values obtained from the polymer database
[b] Value for decanol from Hansen Solubility Parameters: A User's Handbook, Second Edition
[c] Value for decanol from https://www.kabusa.com/Dilectric-Constants.pdf
[d] from Novakov, I. A; Medvedev, V. P; Vaniev, M. A; Medvedev, G. V; Sakibayeva, S. A and Kovaleva, A. Y. Oriental Journal of Chemistry; 2017, **33**, 2297-2302.
[e] From B.T. Smith, Remington Education: Physical Pharmacy, Pharmaceutical Press, 2015
[n/a]: not available

Table S2 Molecular weight range and certificate of analysis as indicated by the supplier.

Matrix	M_n $(g.mol^{-1})$	Given Range $(g.mol^{-1})$	Mn Certificate of analysis $(g.mol^{-1})$
PTHF	250	230-270	269
	650	600-700	652
	1000	950-1050	984
	2000	1900-2100	2033
	2900	2826-3117	2992
PPG	400	*	*
	725	*	*
	2000	*	*
PEG	400	380-420	398
PPD	250	220-280	250
Pripol	537	n/a	n/a
PDMS	5500	*	*
Dec	174	n/a	n/a
HPB	3100	*	*

n/a = not applicable; * not available; # dispersity provided by the supplier