

Supplementary Info

Time-temperature superposition

Time-temperature superposition (TTS) was used to get a broader relaxation spectrum to reveal further dynamics of the ionic networks as well as use the TTS principle to investigate thermal history of the samples. The shift factor (a_T) for the ratio of relaxation times (which under most requirements is equivalent to the ratio of viscosities) at a given temperature (T) to a reference temperature (T_o) is given by the following equation (Zhao et al. 2010):

$$\log_{10} a_T = - C_1(T - T_o) / C_2 + (T - T_o)$$

where C_1 and C_2 are fitting constants according to the WLF theory.

Figures S1 shows TTS shifted dynamic moduli data for several ionic networks formed from DiCOOH-PEG 250 and 600, respectively, with various cross-linkers. The data illustrated in the figure represents data taken over a wide temperature range and which has been shifted to a reference temperature using the principle of time-temperature superposition (TTS). The shift factors used to create the master curves were obtained from least-square analysis of the available data to the WLF equation. As we can observe, the mixture of TAEA and DiCOOH-PEG 250 (Fig. S1(a)) exhibits low elasticity at low frequencies which is typical of an unentangled polymer melt. However, the loss modulus (G'') scales with the frequency to the power 1 over the entire range of frequencies, which is typical for the scaling of a critical gel (Winter and Chambon 1986; Chambon and Winter 1987). There is small plateau in the elasticity (G') at low frequencies and no apparent crossover point over the range of frequencies measured.

The TTS shifted dynamic moduli data for the ionic network formed by the first generation PPI dendrimer (PPI G1) with DiCOOH-PEG 250 are also shown in Fig. S1(b). As can be seen from the plot, the mixture exhibits low elasticity, which is typical of an unentangled polymer melt. There is what appears to be a small entanglement plateau at frequencies above 10 Hz and no apparent crossover point over the range of frequencies measured. It is, however, curious that the elastic modulus does not exceed the loss modulus at the plateau modulus as for melts and networks. This may be explained by the dynamic nature of the cross-linking points which are strongly stress-releasing but at the same time are well-entangled at fast frequencies. In other words the chains

break the ionic bonds rather than relying on reptation, and since the molecular weight of the individual linear polymer chains are below the entanglement weight they rely on Rouse dynamics.

The data for ionic network formed by mixing PPI G2 with DiCOOH-PEG 250 (1:4) is also shown (Fig. S1 (c)). The network has similar behavior to a critical gel where $G'(\omega) \approx G''(\omega)$ for all frequencies but with the slight variation that they are not overlapped but rather $G'(\omega) \approx kG''(\omega)$ where k is a constant. This relationship holds for over 6 decades. This means that there is little effect from microdomains.

So from the data shown here in the SI it is obvious that there are no significant microdomains indicating heterogeneity on the micro scale for the investigated ionic networks.

References:

- Zhao X, Huebsch N, Mooney DJ, Suo Z (2010) Stress-relaxation behavior in gels with ionic and covalent crosslinks. *J Appl Phys* 107 (6):063509-1,063509-5
- Winter HH, Chambon F (1986) Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *J Rheol* 30:367-382
- Chambon F, Winter HH (1987) Linear viscoelasticity at the gel point of a crosslinking PDMS with imbalanced stoichiometry. *J Rheol* 31:683-697

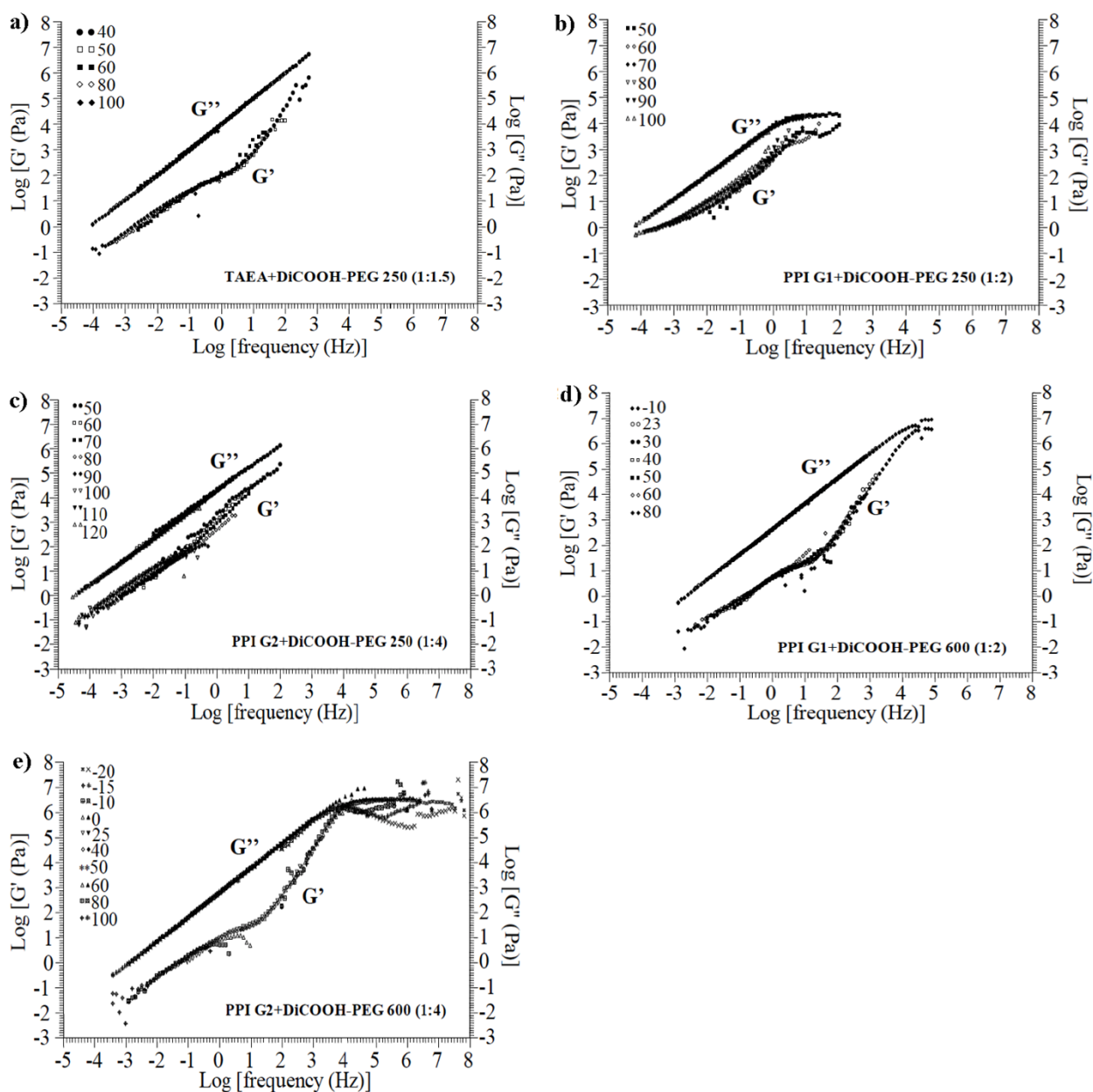


Fig. S1 TTS shifted dynamic moduli data for stoichiometric ionic networks: a) TAEA+ DiCOOH-PEG 250 (1:1.5); b) PPI G1+DiCOOH-PEG 250 (1:2); c) PPI G2+DiCOOH-PEG 250 (1:4); d) PPI G1+DiCOOH-PEG 600 (1:2); e) PPI G2+DiCOOH-PEG 600 (1:4). All of them referenced at 50°C.