The critical role of the interfacial layer in associating polymers with microphase separation

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Abstract:

Polymers with dynamic (transient) bonds, often called associating polymers, have been attracting significant attention in recent years due to their unique viscoelastic properties, self-healing ability and recyclability. Nevertheless, understanding the mechanisms and the factors controlling their macroscopic properties remain limited due to higher complexity introduced by the dynamic bonds. In this study, small angle X-ray scattering (SAXS), broadband dielectric spectroscopy (BDS) and rheology were applied to unravel the structure and dynamics of telechelic associating polymers with different molecular weights. SAXS measurements revealed phase separation of the functional end groups with an average cluster size $\sim 2-3$ nm and the distance between clusters controlled by the chain length. Borrowing the interfacial layer model (ILM) analysis of BDS data from the polymer nanocomposite field, we demonstrated the presence of an interfacial polymer layer with a thickness of $\sim 0.7 - 0.9$ nm surrounding these clusters. Rheological measurements

showed quantitatively that the presence of the interfacial layer significantly alters the viscoelastic behavior of these materials, indicating the crucial role of the interfacial layer in defining the macroscopic mechanical properties of the studied telechelic materials. The presented results emphasize that phase separation of the functional groups in associating polymers leads to very significant changes of the viscoelastic properties, opening a promising avenue in the design of novel functional materials.

Key words:

Associating polymers, Phase Separation, Dielectric spectroscopy, Interfacial layer, Mechanical Reinforcement

Introduction:

Associating polymers are a unique class of polymers possessing functional groups which form a transient network *via* reversible (dynamic) bonds^{1, 2}, such as hydrogen bonds^{3, 4}, ionic bonds^{5, 6}, π - π interaction⁷, metal-ligand bonds^{8, 9} and host-guest interaction¹⁰. Although, these various dynamic bonds have different binding energies, they all are much lower than that of covalent bonds which connect repeating units in polymers¹¹. Currently polymers with dynamic bonds attract significant attention due to their easy recyclability, unique viscoelastic properties¹² and potential use in many applications ranging from super-stretchable and self-healing materials¹³, to shape memory materials.¹⁴ These materials also exhibit extreme toughness and extensibility due to efficient energy dissipation by the dynamic bonds and their rearrangements^{15, 16}.

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The simplest mode of association is binary interaction, in which two complementary functional groups associate together and the dynamics of the polymer is controlled by the lifetime of the associating bond. However, recent studies¹⁷⁻¹⁹ revealed a deviation between the bond lifetime and the macroscopic network relaxation timescale, and this discrepancy can be reasonably well explained by the bond lifetime renormalization model²⁰. In case of immiscibility of functional groups and backbone chains²¹, the functional groups aggregate in clusters, resulting in a microscopic phase separation. Such phase separation has been found in different kinds of associating polymers e.g., in ionomers^{5, 22} or polymers with hydrogen bonding²³, and even in some vitrimers²⁴. The clusters of functional groups can form a solid phase in the polymer melt^{25, 26}, if their glass transition temperature T_g, or melting temperature T_m are higher than T_g of the polymer backbone. Characteristic structure and morphology of these clusters can also be tuned with the architecture of the polymers²⁷. These microphase separated associating polymers show unique viscoelastic behavior, which cannot be captured by the model mentioned above, and no detailed model description exists for these systems.

In heterogeneous polymeric systems, such as polymer nanocomposite (PNC), an interfacial polymer layer with significantly altered structural and dynamic properties exists around the solid nanoparticles^{28, 29}. In the past few years, Broadband Dielectric Spectroscopy (BDS) has been applied to study the interfacial layer in polymer nanocomposites³⁰⁻³⁶. Through model fitting analysis, the quantitative information, including the characteristic relaxation time and thickness of the interfacial layer, can be estimated^{31, 36}. A similar interfacial layer also forms in associating polymers with microphase separation^{5, 37}. In ionomers, the existence of the interfacial layer was confirmed by NMR³⁸ and quasi-elastic neutron scattering,³⁹ and was also characterized by BDS^{40, 41}. This interfacial layer changes rheological properties, dramatically broadens the glass-

to-rubber transition regime and changes the rubbery plateau level⁴². Based on the rheological and dielectric measurements, an existence of the interfacial layer formed around the cluster was also proposed⁴³. However, the interfacial layer in associating polymers has not been studied in detail, as was done in PNC samples.

In this paper, we employed small-angle X-ray scattering (SAXS), BDS and rheology to study structure, segmental relaxation and viscoelastic properties of telechelic associating polymers with poly(dimethyl siloxane) (PDMS) backbone and two different types of associating end groups. Our previous studies revealed strong microphase separation in some of these polymers, which is connected to an unusually high rubbery plateau modulus and demonstrated that their viscosity is controlled by structural relaxation in the clusters of the end groups⁴⁴⁻⁴⁶. There we speculated that the high rubbery modulus might be explained by a higher modulus in the polymer interfacial layer⁴⁶. Here, we present a detailed analysis of the microstructure, the interfacial layer volume fraction and thickness in these systems using approach developed for analysis of the dielectric relaxation spectra in PNCs. We demonstrate that the characteristic inter-cluster distance is defined by the polymer chain length. Presented here analysis of the BDS spectra unambiguously confirms the formation of an interfacial polymer layer surrounding these clusters in all the samples. Moreover, this analysis provides estimates of the interfacial layer thickness that appears rather thin ~ 0.7 -0.9 nm. Finally, we show that microphase separation of the functional groups and formation of this interfacial layer drastically change viscoelastic properties of these materials with extremely broad and high rubbery plateau. Using the interfacial layer thickness, we estimate the modulus in the interfacial layer which almost reaches glassy modulus value.

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Materials and Measurements:

The non-associating methyl terminated PDMS, labelled as PDMS-CH₃ with molecular weights (MW) 900, 2000, 3750 g/mol were purchased from Gelest Inc. and were used without further purification. Telechelic polymers with associating functional groups at both ends were synthesized in our group following the procedures described below.

Synthesis of PDMS-COOH: The synthesis of these polymers was described in details in our previous paper⁴⁴. In brief, the PDMS-COOH (Fig. 1a) was obtained by reacting PDMS-NH₂ (purchased from Gelest Inc.) with succinic anhydride. The reaction was conducted in tetrahydrofuran (THF) under N₂ atmosphere at 40 °C for 2 days, with the catalysis of triethylamine and 4-Dimethylaminopyridine (DMAP). After the addition of hydrochloric acid (HCl) and extraction by dichloromethane (DCM), the final product was dried before tests. ¹H NMR measurements confirmed the final product⁴⁴.

Synthesis of PDMS-UU (Figure 1b): 96 mg (3.1 mmol) methylamine solution (2M in tetrahydrofuran) was added dropwise into 0.4 g (2.4 mmol) hexamethylene diisocyanate dissolved in 10 mL of anhydrous dimethyl sulfoxide in a flame-dried 100 mL round bottom flask. The reaction was carried out at room temperature for 2 hours under continuous stirring in the glove box. The mixture was then added dropwise into 2.28g (0.76 mmol) aminopropyl terminated PDMS (MW = 3,000 g/mol) dissolved in 10 mL of anhydrous dichloromethane (DCM) in a flame-dried 100 mL round bottom flask. The reaction was conducted for 2 days at 40 °C under continuous stirring in the glove box. After dialysis against DCM for two days, the solvent was removed by rotary evaporation. The final product, telechelic PDMS functionalized by urea groups at both ends (Figure 1b), was obtained after drying at vacuum oven. The ¹H NMR spectrum of PDMS-UU is shown in Figure S1 in Supporting Information (SI).

Differential scanning calorimetry (DSC) measurements were performed using a Q2500 DSC from TA Instruments. The samples were dried in vacuum oven at 333 K overnight before placed into the DSC pans. The samples were first equilibrated isothermally at 363 K for 10 minutes to remove the thermal history, and then quenched to 113 K (to avoid crystallization). After equilibration for 10 minutes, the samples were heated up to 363K with a rate of 10K/min. This procedure was repeated twice for each sample to ensure the repeatability.

Small and wide-angle X-ray Scattering (SAXS and WAXS) spectra of all the samples were measured using an in-house setup of the Laboratoire Charles Coulomb, "Réseau X et gamma", Université Montpellier, France. A high brightness low power X-ray tube, coupled with aspheric multilayer optic (GeniX3D from Xenocs) delivered an ultralow divergent beam (0.5 mrad, flux 35 Mphotons s⁻¹, λ =1.5418 Å). The scattered intensity was measured by a 2D pixel Pilatus detector with a sample-to-detector distance of 0.2 m. Samples were prepared in glass capillaries. All intensities were corrected for transmission and the empty cell contribution was subtracted. The measurements were performed at room temperature.



Figure 1 (a) the chemical structure of PDMS-COOH **(b)** Synthesis of (Double Urea)-Terminated Polydimethylsiloxane (PDMS-UU) from Amine-Terminated Polydimethylsiloxane (PDMS-NH₂).

Broadband dielectric spectra (BDS) in the frequency range 10^{-2} - 10^{6} Hz were measured using a Novocontrol system that includes an Alpha-A impedance analyzer and a Quatro Cryosystem temperature control unit. The PDMS-UU sample was placed between two gold-plated electrodes with diameter of 20 mm, separation between electrodes was 174 µm. PDMS-COOH samples were placed into a parallel-plate dielectric cell made of sapphire and invar steel with an electrode diameter of 12 mm. A capacitance of 20 pF was obtained for the cell with an electrode separation of 50 µm. PDMS-CH₃ sample was placed into a parallel-plate dielectric cell made of sapphire dielectric cell made of sapphire and invar steel with an electrode diameter of 10 mm. A capacitance of 3.3 pF was obtained for the cell with an electrode separation of 210 µm. To prevent crystallization, all the samples were quenched from room temperature to about 113 K and reheated to 10 K below the glass transition temperature T_g before the measurements. The spectra were measured on heating. After each

temperature increase, the samples were equilibrated for 10 minutes to reach thermal stabilization within 0.1 K. Only PDMS-CH₃ and PDMS-COOH (DP 74) samples showed signs of crystallization, and they were measured on heating until crystallization. Measurement of their dielectric spectra during heating and cooling in the temperature range below crystallization confirmed repeatability of the data and ruled out influence of crystallization on the measured spectra. All other samples did not have crystallization, and were measured on heating up to ~300K and then on cooling back to ~T_g to confirm reproducibility of the data.

The viscoelastic properties were probed by small-amplitude oscillatory shear (SAOS) measurements through a strain-controlled mode of the AR2000ex (TA Instruments) in an angular frequency range of 10^{-1} – 10^2 rad/s using parallel plate geometry, with a disk diameter of 4mm. The gap between plates was ~ 0.6 - 0.7 mm for all the samples. The samples were quenched to a temperature near T_g before a frequency sweep was conducted at several different temperatures on heating. Prior to each frequency sweep measurement, the samples underwent thermal stabilization for 5 minutes to make sure that thermal equilibrium has been reached.

Results

1. X-ray scattering

The X-ray scattering spectra of all the samples exhibit a strong and sharp peak at q ~ 0.85 Å⁻¹ which reflects spatial correlations between PDMS segments, along with a weaker peak around q ~ 1.5 Å⁻¹ which reflects intra-segmental correlations⁴⁷ (Fig. 2a). The low-q peak around 0.1 Å⁻¹ can be found in spectra of both PDMS-COOH and PDMS-UU samples, while no such peak is visible in the spectra of the non-associating PDMS-CH₃ reference sample. Hence this low-q peak

is a clear indication of a microphase separation in the former systems. The peak position q_c provides a rough estimate of the average center-to-center distance between the clusters³⁷, $d \approx \frac{2\pi}{q_c}$, and its intensity should indicate the extent of aggregation.



Figure 2. (a) Small and wide angle X-ray scattering results for all telechelic associating polymers of different degree of polymerization (DP) and PDMS-CH₃ as indicated. The data are offset vertically for clarity. The arrows indicate the low-q peak position. (b) The same X-ray scattering results normalized with respect to the PDMS backbone peak after subtracting a baseline.

To analyze the intensity of the low-q peak, all the spectra were normalized to the high-q peak of the PDMS backbone after subtracting a baseline (Fig. 2b). Then the low-q peak was fitted using a Gaussian peak function (Fig. S3):

$$I(q) = \left(\frac{A}{w\sqrt{\pi/2}}\right) \exp\left[-\left(\frac{q-q_{c}}{w}\right)^{2}\right]$$
(1)

where A is the intensity of the peak defined by the amount of clusters present and their contrast, i.e. the difference of scattering length density between end groups and backbones, w is the width and q_c is the position of the peak. For polymers with shorter chains, the volume fraction of end

groups f_{els} not negligible, and the obtained A value from fitting needs a correction by the the factor $(1 - f_e)$. Here we assume that the volume fraction of the end groups is the same as their weight fraction, i.e. the density of the end group clusters is about the same as the PDMS density. Thus, $A(1 - f_e)$ is considered as the correct normalized intensity of the low-q peak, that represents the total amount of end groups in the clusters. Indeed the amplitude of the peak increases with the increase in end group weight fraction (Table 1). Assuming that all functional groups are phase separated to the clusters, we can roughly estimate an average cluster radius using the relationship for a cubic arrangement of spherical particles ⁴⁸: $R_{cluster} = \frac{d}{2} (\frac{6}{\pi} f_e)^{\frac{1}{3}}$. Table 1 presents the cluster center-to-center distance, cluster radius and the normalized intersity of the low-q peak estimated from the SAXS data. The cluster radius appears to increase slightly with the decrease in the backbone DP.

2. Broadband Dielectric Spectroscopy:

The BDS spectra of the studied telechelic associating polymers exhibit several relaxation processes^{44, 45, 49, 50}. We focus here on a detailed analysis of the PDMS segmental relaxation spectra (Figs. 3, 4). Direct comparison of the dielectric loss spectra of a telechelic associating polymer with its non-associating counterpart at the same temperature shows not only a significant shift of the peak position but also a decrease in its amplitude (Fig. 3a). In addition, the amplitude of the segmental relaxation peak decreases strongly with decreasing degree of polymerization (DP) of the telechelic associating polymers (Fig. 3b). The other remarkable observation is that the peak broadens significantly for the polymers with associating end groups, and the broadening increases drastically with decrease in DP (Fig. 3b) and upon cooling (Fig. 4a). The observed changes in the BDS spectra are very similar to the ones observed in polymer nanocomposites (PNCs)^{34, 51}. Moreover, the low frequency side of the segmental peak appears

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different for UU and COOH terminated chains (Fig. 4b). An additional dielectric process is obvious in the spectra of PDMS-COOH with DP=50 (Fig. 4b). It was called α^* -relaxation and was assigned to binary association of the functional groups⁴⁴.



Figure 3. Dielectric loss spectra $\varepsilon''(v)$ for (a) PDMS-COOH and PDMS-CH₃ with DP=50 at 155K. (b) PDMS-COOH with DP=13 at 168K, DP=22 at 164K and DP=50 at 161K. The arrow indicates the decrease in the amplitude of segmental relaxation (α -process). Temperatures were chosen to have the segmental peak in the same frequency range.

Table 1: Degree of polymerization (DP), Number of Kuhn segments (N_k) , Molecular weight of the PDMS associating polymers including end groups (M_n) , weight fraction of the end groups (f_e) , center-to-center distance between clusters (d), radius of clusters $(R_{cluster})$ and corrected intensity of the low-q peak A(1- f_e)

Material	DP	N _k	M_n (kg/mol)	f_e (wt%)	d (nm)	$R_{cluster}$ (nm)	$A(1-f_e) (a.u.)$
PDMS-COOH	13	4	1.28	24.7	4.08	1.59	46.8
	22	7	1.94	16.3	4.43	1.50	32.3
	50	16	4.02	7.9	5.12	1.36	23.2
	74	23	5.57	5.7	5.97	1.43	16.2

PDMS-UU	50	16	4.21	12.2	5.70	1.75	7.45



Figure 4. Normalized dielectric loss spectra vs. normalized frequency of the α -relaxation of (a) PDMS-COOH DP=13 from 166K to 180K with 2K increment. (b) PDMS-COOH, PDMS-UU and PDMS-CH₃ with DP=50. The small peak at lower frequencies in PDMS-COOH spectra is assigned to binary association (a*-process)⁴⁴.

To estimate the relaxation time, the loss spectra were initially fit to a single Havriliak-Negami

(HN) function⁵²:

$$\varepsilon''(v) = Im\left\{\frac{\Delta\varepsilon}{[1+(2\pi i v\tau)^{\alpha}]^{\gamma}}\right\}$$
(2)

in which $\Delta \varepsilon$ denotes the dielectric relaxation strength, α and γ are the shape parameters. τ is HN relaxation time that is related to the relaxation time at the loss maximum τ_{max}^{52} :

$$\tau_{max} = \tau \left[\sin \left(\frac{a\pi}{2+2\gamma} \right) \right]^{-\frac{1}{a}} \left[\sin \left(\frac{a\gamma\pi}{2+2\gamma} \right) \right]^{\frac{1}{a}}$$
(3)

The latter is often used as the characteristic segmental relaxation time in polymeric materials. The obtained τ_{max} follows the Vogel–Fulcher–Tammann (VFT) equation (Fig. 5a).

$$\tau_{max} = \tau_0 \exp(\frac{B}{T - T_0}) \tag{4}$$

Here τ_0 is a limiting relaxation time, B and T_0 are material dependent parameters. By extrapolating τ_{max} to $\tau \approx 100$ s, the glass transition temperatures (T_g) from the dielectric measurements are estimated. It is comparable to the calorimetric T_g (Fig. 5b), confirming the assignment of the fastest relaxation process in BDS to the segmental motion of the PDMS backbone. The addition of the functional groups at the chain ends shifts the segmental relaxation time and T_g of the backbone, with stronger shift for shorter chains. Changing the functional end group of the DP=50 samples does not affect segmental dynamics and T_g significantly.



Figure 5. (a) Activation plot of the dielectric α -relaxation time of PDMS-COOH and PDMS-UU (closed circles) along with their non-associating counterparts PDMS-CH₃ (open circles) with different DP. The solid and dotted lines are VFT fits to the respective data sets. **(b)** Glass transition temperature (Tg) vs. total molecular weight including end groups (Mn) for PDMS-COOH and PDMS-UU (closed symbols) as well as their non-associating counterparts PDMS-

CH₃ (open symbols). Squares with error-bars - results from BDS; circles - results from DSC. The lines are guides for the eye.

The broadening of the segmental relaxation peak clearly depends on the chain length, i.e. DP of the samples (Figs. 3b, 6). While the sample with DP=74 shows only a weak broadening on the low frequency side in comparison to the spectrum of PDMS-CH₃, the extent of broadening is significant for DP=13 sample (Fig. 6). In the case of DP=13, the broadening can even be found on the high frequency side, indicating extremely broad distribution of relaxation times in systems with short chains. In analogy to PNCs, we ascribed the broadening of the spectra to the formation of an interfacial layer.



Figure 6. Normalized dielectric loss spectra vs. normalized frequency of the α -relaxation for PDMS-COOH (blue symbols) and PDMS-CH₃ (black symbols) with DP=74, 22 and 13.

3. Shear rheology

To analyze the effect of phase separation on the viscoelastic properties of these samples, we constructed master curves from the shear modulus spectra using time-temperature superposition (TTS). The results for storage (G') and loss (G") moduli for PDMS-UU sample are shown in Figure 7 together with earlier results for PDMS-COOH samples^{44, 46}.



Figure 7. Storage (closed symbols) and loss (open symbols) shear moduli master curves for all associating polymers studied here. The reference temperature is taken as 158K for the PDMS-COOH (DP=13) sample. The curves of the other samples are horizontally shifted to match the position of the segmental relaxation peak. The vertical arrow indicates the increase in plateau modulus with decrease in DP value from 74 to 13. The horizontal blue dashed line indicates the rubbery plateau modulus level for the PDMS-COOH (DP 22) sample.

All the samples demonstrate the prominent rubbery plateau regime. The plateau modulus value is determined as $G_{pl} = G'(\omega_{min})$, where ω_{min} is the frequency of the loss modulus minimum, $G''(\omega_{min})$, in the rubbery region⁵³. For the PDMS-COOH samples, the plateau modulus is elevated, and its range extends dramatically with decreasing DP. For the DP=74 and DP=50 samples, the plateau modulus is ~1 MPa, a usual range for rubbery materials, but it increases strongly for samples with smaller DP, reaching around 100 MPa for DP=13 (Fig. 7). The latter is

only an order of magnitude lower than the glassy modulus. The PDMS-UU sample shows a higher modulus than PDMS-COOH with the same DP=50, and it shows the longest rubbery plateau of any studied sample. The latter can be explained by the higher thermal stability of the clusters formed by the urea groups that is evident from the higher second T_g of the PDMS-UU sample (Fig. S2b) compared to PDMS-COOH samples (Fig. S2a). This second T_g is assigned to the structural relaxation in the clusters of associating groups, which is $T_{g2} \sim 280$ K in UU clusters, while it is $T_{g2} \sim 190$ K in COOH clusters⁴⁴.

Discussion

Analysis of the SAXS data clearly demonstrates that the decreasing DP, i.e. increasing weight fraction of associating chain ends, leads to an increase in amplitude of the low-q peak, a decrease in the distance between clusters d, and a slight increase in the radius of the clusters $R_{cluster}$ (Table 1). For the PDMS-UU sample $R_{cluster}$ is larger than in the PDMS-COOH sample with the same DP=50 due to the larger size of the double-urea end groups (Fig. 1).

It is expected that the distance between clusters should be controlled by the end-to-end distance of the PDMS backbone R_{ee} because the chain should extend from the surface of one cluster to the surface of another adjacent cluster. The value of unperturbed R_{ee} can be estimated using the classical approximation⁵⁴:

$$\langle R_{ee} \rangle = l_k \sqrt{N_k} \tag{5}$$

Here, $l_k \approx lC_{\infty}$ and $N_k = \frac{n}{c_{\infty}}$ are the length and the number of the Kuhn segments, respectively. l = 0.164 nm is the length of the Si-O bond, $C_{\infty} = 6.3$ is the characteristic ratio for PDMS⁵⁵, and n

= 2*DP is the number of backbone bonds. Real Ree of a chain will depend on positions of its end groups in two clusters. The shortest average distance between two surfaces of adjacent clusters is $\sim d - 2R_{cluster}$. But it is unlikely that many connecting chains will have the minimum length. The reason is that there are many chain ends per cluster^{44, 46} and most of them will be distributed across the entire surface of the cluster. Naively, we would expect that the average Ree for all the chains connecting two neighbor clusters should be between $\sim d - R_{cluster}$ and $\sim d$. Analysis shows that the unperturbed average end-to-end distance of the polymer chains is shorter than d -Rcluster for chains with small DP, and is in the range between d - Rcluster and d for larger DP (Fig. 8). It is interesting that, although d and R_{cluster} are larger in the PDMS-UU system than in the PDMS-COOH system with the same DP=50, d - R_{cluster} is essentially the same, emphasizing that this distance indeed depends on Ree. We note that similar studies of telechelic polyisobutylene revealed that the equilibrium Ree can be comparable and even larger than the distance between clusters d³⁷. However, the molecular weight of the studied polyisobutylenes was much higher (up to 30kg/mol)³⁷. Thus, analysis of the SAXS data (Fig. 8) suggests that the chains in the systems studied here might be stretched especially at smaller DP. In addition, the increased amplitude of the highest-q peak observed in the normalized X-ray scattering with a decrease in DP (Fig. 2b) is also a sign of chain stretching. According to the earlier studies⁴⁷, intensity of the higher q peaks in PDMS depends on population of the gauche conformational states.



Figure 8 Center-to-center distance between clusters d (open circles), $d - R_{cluster}$ (closed squares) and $d - 2R_{cluster}$ (open traingles) distances as a function of DP for PDMS-COOH (black symbols) and PDMS-UU (red symbols) systems. The dashed line presents the calculated unperturbed PDMS end-to-end distance.

In analogy with the well-known case of PNC, we can ascribe the observed behavior of the dielectric and rheological spectra to the existence of an interfacial polymer layer surrounding the "glassy" clusters of the associating chain ends. In our earlier studies⁴⁶ we used this idea to estimate a possible thickness of the interfacial layer using the plateau modulus by *assuming* the modulus in the interfacial layer to be ~ 1 GPa. However, the BDS spectra provide an independent approach to estimate the thickness of the interfacial layer^{31, 32, 35}. Knowing the thickness of the interfacial layer, we will be able to *determine* its modulus from the rheological data (Fig. 7).

Several approaches to fit the dielectric spectra had been applied to decipher the contribution from an interfacial layer in heterogeneous systems such as PNCs^{31-33, 35, 56, 57}. Previously, a simple two HN functions fit (an additional HN function to represent the interfacial layer process) and a more convoluted interfacial layer model (ILM) have been used to study the interfacial layer properties

in PNCs³¹. The ILM is the more accurate method to study the interfacial layer using BDS since it considers the non-additive feature of the dielectric response in heterogeneous systems⁵⁶. Although the two HN functions approach is less accurate³¹, it is much simpler and has been utilized in quite a few studies^{32, 33, 57} providing reasonable results. Thus, we chose the simpler 2-HN functions approach to analyze the dielectric segmental relaxation spectra in studied here associating polymers. To account for the additional α *-relaxation process, we added a third HN function to fit the dielectric spectra:

$$\varepsilon''(\upsilon) = Im \left\{ \frac{\Delta \varepsilon_{bulk}}{[1 + (2\pi i \upsilon \tau_{bulk})^{\alpha_1}]^{\gamma_1}} + \frac{\Delta \varepsilon_{int}}{[1 + (2\pi i \upsilon \tau_{int})^{\alpha_2}]^{\gamma_2}} + \frac{\Delta \varepsilon_{\alpha*}}{[1 + (2\pi i \upsilon \tau_{\alpha*})^{\alpha_3}]^{\gamma_3}} \right\}$$
(6)

Here $\Delta \varepsilon_{bulk}$, $\Delta \varepsilon_{int}$ and $\Delta \varepsilon_{\alpha^*}$ are the dielectric relaxation strengths of bulk-like PDMS segments, segments in the interfacial layer, and of the binary association process (α^* process), respectively. τ_{bulk} , τ_{int} and τ_{α^*} are the corresponding HN relaxation times; α and γ represent the shape parameters for their respective processes. To reduce the number of free fit parameters, we fixed the shape parameters for bulk-like PDMS segments (α_1, γ_1) to the values from the fit of nonassociated PDMS-CH₃ spectra. The other parameters remained free. Representative fits of the dielectric loss spectra to the eq. 6 for all the samples are shown in Fig. 9.



Figure 9. Dielectric loss spectra $\varepsilon''(v)$ for (a) PDMS-COOH DP 13 at 176K, (b) PDMS-COOH DP 22 at 169K, (c) PDMS-COOH DP 74 at 163K, (d) PDMS-COOH DP 50 at 163K, (e) PDMS-UU DP=50 at 164K. The red solid lines are the fits with three HN functions. The pink, brown and blue dashed lines are the individual contributions of the α , interfacial and α^* relaxation processes, respectively.

Analysis of the results reveals (Fig. 10a) that segmental relaxation in the interfacial layer is approximately one order of magnitude slower than in the bulk-like polymer. Interestingly, the ratio τ_{int} to τ_{α} is about the same for all the samples, which is rather independent of temperature as well (Fig. 10b). We note that the segmental relaxation time in the interfacial layer was found to be about one order of magnitude slower than that in the bulk polymer also in PNCs^{30, 31} and polymer grafted nanoparticle samples (PGN)⁵⁸. However, it was shown that in the case of nanocomposites, the slowdown of segmental dynamics in the interfacial layer depends on the particular polymer-nanoparticles interactions^{59, 60}.



Figure 10. (a) Activation plot of the segmental relaxation time in the bulk-like PDMS (pink), in the interfacial layer (brown) and the α^* (blue) relaxation time in PDMS-COOH DP 50 sample. (b) The ratio between the relaxation times of the interfacial layer and bulk-like PDMS segments for the studied systems.

The fit results of the dielectric spectra also demonstrate that the amplitude (relaxation strength) of the bulk-like process decreases and that of the interfacial layer increases gradually with decreasing DP, implying an increasing volume fraction of the interfacial region with decrease of the chain length (Figs. 9). In the case of the sample with DP=13, almost the entire relaxation spectrum is assigned to the interfacial layer process. Quantitative analysis of the dielectric relaxation strength of the segmental peaks revealed that the bulk-like segmental peak in associating polymers, $\Delta \varepsilon_{bulk}$, is always lower than that in the non-associating polymers, $\Delta \varepsilon_{nonass}$, (Fig.11). For all the non-associating PDMS, the values of $\Delta \varepsilon_{nonass}$ increase upon

cooling, following Curie's law (Fig. 11). However, $\Delta \varepsilon_{bulk}$ in telechelic polymers shows a much weaker temperature dependence. Moreover, the sample with DP=22 exhibits essentially no temperature dependence of $\Delta \varepsilon_{bulk}$, while $\Delta \varepsilon_{bulk}$ even decreases upon cooling in sample with DP=13. These observations are similar to the results known from PNCs, and interpreted as an increase of the interfacial layer thickness upon cooling^{58, 61}. This also explains the observed increase in the broadening of the segmental relaxation peak upon cooling (Fig. 4a).



Figure 11. Temperature dependence of the dielectric relaxation strength $\Delta \varepsilon$ of the α -relaxation of the bulk-like PDMS part in telechelic associating polymers (closed circles) and α -relaxation of the PDMS-CH₃ (open circles).

It is now well documented that the dielectric strength of the segmental relaxation in the interfacial layer, $\Delta \varepsilon_{int}$, of thin polymer films and PNCs is strongly suppressed^{31, 58, 62}. It was ascribed to a strong restrictions on segmental reorientation in the crowded interfacial layer⁵⁸. Thus, $\Delta \varepsilon_{int}$ does not reflect the true volume fraction of the polymer interfacial layer⁵⁸, and one

should use $\Delta \varepsilon_{bulk}$ to estimate the volume fraction of the bulk-like polymer, $\varphi_{bulk}^{31, 58}$. Then the interfacial volume fraction can be estimated using $\varphi_{int} = 1 - \varphi_{NP} - \varphi_{bulk}$, where φ_{NP} is the volume fraction of nanoparticles in the PNC sample. Following this approach, we use $\Delta \varepsilon_{bulk}$ to calculate the volume fraction of the bulk-like polymer, and then the volume fraction of the interfacial layer:

$$\varphi_{int} = 1 - f_e - \frac{\Delta \varepsilon_{bulk}}{\Delta \varepsilon_{nonass}} \tag{7}$$



Figure 12. Variation of the volume fraction (a) and the thickness (b) of the interfacial layer vs. inverse temperature for the studied telechelic associating polymers.

The estimated volume fraction of the interfacial layer ranges from 20% to 40%, as DP decreases from 74 to 22, and reaches 70% for the sample with DP=13 (Fig. 12a), indicating the strong dominance of the interfacial layer in this sample. Using the estimated φ_{int} and assuming a

spherical shape of the chain end group aggregates, we can calculate the interfacial layer thickness using the equation³¹:

$$l_{int} = R_{cluster} \times \left[\left(\frac{\varphi_{int} + f_e}{f_e} \right)^{\frac{1}{3}} - 1 \right]$$
(8)

The analysis (Fig.12b) reveals that the interfacial layer thickness ranges from 0.7 to 0.9 nm for all telechelic polymer samples studied here, essentially independent of the backbone DP or chemistry of the end group. This value is much smaller than the interfacial layer thickness found in the PNCs³⁴. We explain this result by much smaller cluster size with R_{cluster} \sim 1.4-1.8 nm, while in PNCs usually nanoparticles have R \sim 10-20 nm. However, this thickness is consistent with the earlier assumption⁵ that it should be comparable to the polymer segment size.

As next step, we analyze the mechanical relaxation spectra (Fig. 7). Classical rubber elasticity theory predicts that the rubbery plateau modulus should be inversely proportional to the molecular weight of the PDMS backbone, M: $G_N = \frac{\rho RT}{M}$. Analysis of the experimental data for the longest PDMS chain with DP=74 revealed that the obtained plateau level is only slightly (~2 times) higher than expected from the classical theory (Fig. 13). However, the difference increases strongly with decreasing DP, reaching ~100 times for the sample with DP=13. As it was shown in our earlier analysis⁴⁶, this difference cannot be explained by a hard-filler effect due to the presence of the glassy clusters. This difference clearly indicates that the interfacial layer has a much higher modulus than the bulk-like PDMS matrix. Here, we use again the analogy to PNCs, especially to polymer grafted nanoparticles. The clusters of chain end groups indeed can be considered as nanoparticles with grafted chains. To analyze the data, we employed the mechanical interfacial layer model used to describe the properties in PNCs, which provides a relationship between the interfacial layer thickness and modulus as well as the macroscopic

mechanical strength of the composite material⁶³. It assumes a non-slippery condition at the bulk polymer - interfacial layer and interfacial layer - filler boundaries. In the model, the shear modulus of the sample G_c is calculated as:

$$40(G_c/G_m)^2|X| + \left(\frac{G_c}{G_m}\right)\{2|Y| + 8|Z|\} - 5|T| = 0$$
(9)

where |X|, |Y|, |Z| and |T| are the determinants of 10×10 matrices which depend on the shear moduli, Poisson's ratios and volume fractions of filler (i.e., end group clusters), interfacial layer and bulk-like matrix, respectively. The full expression of each matrix can be found in Maurer et al.⁶³.

To analyze the mechanical reinforcement, we used the mechanical ILM with the interfacial layer thickness taken from the BDS measurements (Fig. 12b). We assumed that the Poisson's ratio and the modulus of the functional group cluster are the same as in the hydrogen bonding system glycerol⁶⁴, i.e. ~ 0.33 and 3GPa, respectively. The Poisson's ratio of the PDMS matrix and of the interfacial layer were assumed to be 0.495, the same as that of neat PDMS⁶⁵. The shear modulus of the bulk-like PDMS matrix is assumed to follow the classical rubber theory.

The interfacial layer in DP=13 sample occupies essentially the entire polymer fraction (Fig. 12a). Thus, the modulus of the interfacial layer even above the PDMS matrix T_g should be comparable to the measured rubbery plateau level in this sample, i.e. ~100 MPa. Indeed, the best agreement between the plateau modulus level and the mechanical ILM estimates for DP=13 sample is reached (Fig. 13). Using this value, a reasonable agreement of the mechanical ILM predictions and the measured plateau modulus is achieved for all other DPs (Fig. 13). The decrease in the PDMS backbone length leads to an increase in the volume fraction of associating group clusters and to a significant increase in the interfacial volume fraction (Fig. 12a). As a result, the

microphase separation of the associating groups leads to a significant mechanical reinforcement with the rubbery modulus of the shortest chains almost reaching a glass-like modulus value. The reason for so high modulus even at temperatures above the PDMS T_g most probably is related to strong stretching of the chains in the interfacial layer. The estimates show that each cluster contains ~ 35-50 chain ends⁴⁶, which would correspond to a grafting density ~ 1.5 chains/nm². This is significantly higher than in polymer grafted nanoparticles, where the grafting density is usually ~0.5 chains/nm² ⁶⁶. Such a high grafting density leads to a strong crowding and stretching of the chains in the interfacial layer, leading to their restricted flexibility and high modulus.



Figure 13. Plateau modulus of the studied telechelic associating polymers from rheology measurements (black squares) and calculated from the ILM based on the layer thickness estimated from BDS measurements (green squares) as a function of the weight fraction of the end groups. The black dotted line indicates the relationship between plateau modulus and the weight fraction of end groups according to classical rubber theory. The red dashed line is a trend line guided by the datasets.

Thus, BDS and rheological data provide a clear indication of the interfacial polymer layer formed around the clusters of associating end groups. Although this interfacial layer is extremely thin (\sim 0.7 – 0.9 nm), it plays a significant role in relaxation and mechanical properties of associating polymers with phase separated functional groups. The impact of this interfacial layer on the macroscopic properties increases with decreasing chain length due to the increasing volume fraction of the interfacial region. The presented analysis provides a consistent description of both BDS and rheological data for samples with several chain lengths and two different end groups.

Conclusion:

The detailed analysis of the SAXS data of the telechelic polymers studied here reveals that all of them form aggregates of the associating end groups. This result is consistent with the presence of two T_g s observed in DSC. Moreover, the SAXS data provide a direct estimate of the average distance between the aggregates and allow an estimate of their size. Our analysis suggests that the chain end-to-end distance controls the average distance between aggregates, and aggregates containing ~30-55 associating groups increase in size with the decrease in the backbone length. At the same time, BDS and rheological data clearly indicate the existence of an interfacial polymer layer surrounding these clusters with relaxation behavior and mechanical properties different from that of the bulk-like polymer.

To analyze the properties and the thickness of the interfacial layer, we employed models developed for polymer nanocomposites. Indeed, structurally the studied samples are analogous to polymer grafted nanoparticles. Using this approach, we found that the segmental dynamics in the

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interfacial layer is about an order of magnitude slower than that in the bulk-like polymer. The estimated thickness of the interfacial layer is surprisingly small ~0.7-0.9 nm, comparable to a length of a single segment. However, this might be reasonable considering the very small size of the aggregates with $R_{cluster} \sim 1.4 - 1.8$ nm. Using the estimated interfacial layer thickness and the value of the rubbery plateau, we were able to estimate the shear modulus in the interfacial layer. It appears rather high ~ 100 MPa (even at temperatures well above the polymer's T_g), which we explain by a significant chain stretching in this interfacial layer.

Thus, the models employed here provide a consistent description of both BDS and rheological data. We emphasize that the employed here analogy with PNC, especially with polymer grafted nanoparticles, yields a suitable approach for describing and predicting properties of polymers with phase separating associating groups. This advances our understanding of polymers with dynamic bonds which is critical for a rational design of novel functional materials with strongly enhanced viscoelastic properties.

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Supporting Information

The Supporting Information is available free of charge at (website to be determined) and presents NMR, DSC, and fit of the SAXS results.

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