

Low-Frequency Elastic Plateau in Linear Viscoelasticity of Polyelectrolyte Coacervates

Huiling Li¹, Ying Liu¹, Abhishek Shetty², Ronald G. Larson^{1,3}

¹*Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, MI 48109*

²*Rheology Department, Advanced Technical Center, Anton Paar USA Inc., Ashland, VA 23005*

³*Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109*

Abstract

A thorough study is made of the dependences on salt concentration and polymer chain lengths of the low-frequency plateau of coacervates of poly (diallyl dimethyl ammonium chloride), PDADMAC, and poly (sodium 4-styrenesulfonate), PSS. The reliability and reproducibility of these measurements are carefully checked by determining the frequency-dependent stress limits of the rheometer through use of reference fluids, and by repeat experiments with coacervates. Long-time frequency sweeps show that coacervates with less salt are more repeatable than those with higher salt. A low-frequency plateau only reliably appears below a critical salt concentration, and the magnitude of the plateau depends strongly on salt concentration and on chain lengths of both polycation and polyanion. It is only present for molecular weight of the PDADMAC polycation higher than 100kDa, but the magnitude of plateau is more strongly influenced by the chain length of the polyanion, PSS. Possible causes of the low-frequency plateau are discussed.

I. Introduction

Polyelectrolyte coacervates (PECs), which are polymer-rich phases formed by mixing oppositely charged polyelectrolyte solutions, are increasingly applied in coatings, water treatment, personal care products, drug delivery, and other applications [1][2][3][4]. Nevertheless, fundamental understanding of coacervate physical properties, micro-structure, and rheology remains limited [5]. While the pace of measurements of the rheology of coacervates has rapidly increased in recent years [6], clear trends are generally found only within a limited set of materials, and typically only within a given laboratory, with little lab-to-lab cross comparisons of data for the same materials. In particular, some coacervate measurements show “liquid-like” terminal behavior at low frequency [7][8], while others show a “gel-like” behavior [9][10][11][12][13][14]. At low frequency, the latter are characterized by a plateau or near plateau in G' while the former shows a steep decrease in G' with power-law exponent near the expected “terminal” value of 2, or at least

greater than 1. The “gel-like” modulus is often very low (i.e., < 1 Pa), however, leading authors to question whether it lies outside of various sources of error, e.g., the minimum torque, the precision of the phase angle measurement, etc. [9]. In other cases, the plateau is much more prominent and salt-concentration and salt-type dependent [13][14]. In addition, the measurements are typically made on samples extracted following phase separation, wherein a supernatant liquid is removed after mixing, centrifugation, and waiting for equilibration of phase separation. The time periods involved in these steps are often not given, and the order of mixing, when its effect is investigated, is sometimes found to be important [15]. In addition to possible effects of the rheometer-loading procedure on measurement reproducibility, such as variations in how the sample is pressed into the gap, and how it is trimmed, the samples contain water, making them prone to evaporation or be affected by the humidity of the testing environment. Careful checks of measurement reproducibility are rarely reported. In addition, most studies are carried out on commercial samples of high or unknown polydispersity. In these ways and more, it is fair to say that rheological studies on polyelectrolyte coacervates are often “not up to the standards” of rheological studies of more conventional polymers, or of single polyelectrolytes.

While we cannot address all of these issues here, we do propose to study in some detail the limits of rheometer accuracy, reproducibility, and robustness with respect to sample mixing, duration of rheological tests, and repeat measurements of the same loaded samples, different sample loadings, repeated sample preparations, and repeated measurements in different laboratories. We find that while typical rheometric methods have been sufficient to establish some generally valid trends already presented in the literature, many samples we report on here show unusual behavior and limited reproducibility that, if not overcome, limit precise comparisons of data on different samples and from different labs. This is especially true of samples that produce low-frequency “gel-like” plateaus. Since these samples are by definition solids, it is perhaps not surprising that such samples are slow to equilibrate and sensitive to preparation conditions.

The polyelectrolyte samples that we chose for this study are ones that are easily available commercially and widely used in previous studies, that have been found to produce a low-frequency plateau under some conditions of salt and molecular weight [14], namely poly (sodium 4-styrenesulfonate) (PSS) and poly (diallyl dimethyl ammonium chloride) (PDADMAC). We note that given the number of samples and repeat runs we made here, we have chosen not to focus on possible issues related to sample polydispersity or purification. Once work establishing “best practices” and pitfalls of coacervate preparation and measurement are addressed, important issues of polyelectrolyte molecular weight distribution, and quality of synthesis, purification, and characterization should be addressed. We simply note here that any problems related to these latter factors in our work is common to the field at large and to most published papers in the area.

II. Materials and Method

A. Materials

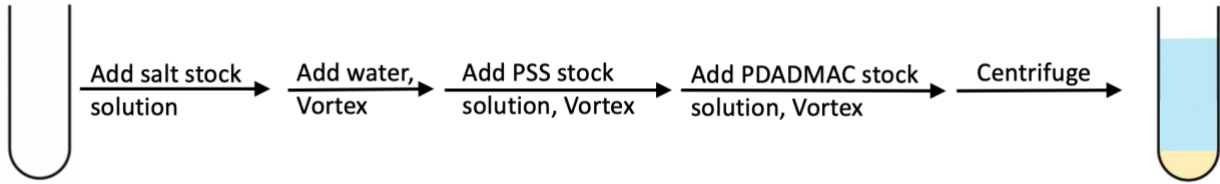
Poly (sodium 4-styrenesulfonate) solutions (PSS) having molecular weights (MWs) of 70kDa (20wt% in water) and 200kDa (30wt% in water), as well as solutions of poly (diallyl dimethyl ammonium chloride) (PDADMAC) with MW <100kDa (35wt% in water), MW 200-350kDa (20wt% in water) and MW 400-500kDa (20wt% in water), were purchased from Sigma-Aldrich. Another less polydisperse PSS (PDI=1.19) was purchased from Scientific Polymer Products, Inc. with MW of 2242kDa in powder state. The certificated standard mineral oil is provided by Anton Paar Inc with a viscosity of 3mPa·s at 20°. The standard viscoelastic PDMS solution with a kinematic viscosity of approx. 1000000 mm²/s (called “AK 1 Million” from Wacker), which corresponds to a dynamic viscosity of roughly 10³ Pas. The molecular weight ranges mentioned above are given by the suppliers. For convenience, we will refer to the PDADMAC materials as “100kDa,” “200kDa,” and “400kDa,” samples, respectively. The materials were used, as has been common, without further purification or characterization. These polyelectrolytes with concentrations of 35 wt%, 30 wt% and 20 wt% in water were diluted to make stock solutions with monomer molar concentrations of 2M, 1.6M and 1.2M, respectively. PSS with MW 2242kDa was prepared at 0.4mol/L by dissolving the powder in water. NaCl stock solutions (5M) were prepared by dissolving crystalline NaCl (Sigma-Aldrich) into water at 25 °C. All water was filtered through a Milli-Q water purification system (Thermo Scientific, MicroPure UV/UF) producing water with a resistivity of 18.1 MΩ·cm at 25 °C.

B. Coacervate Preparation

PECs were formed by mixing cationic and anionic stock solutions at a 1:1 stoichiometric ratio of monomer repeat units with salt solutions, as shown in Scheme 1. Concentrations and volumes were chosen to achieve overall polycation and polyanion monomer concentrations of 0.1M each (0.2M total monomer concentration) in the final mixture (but before phase separation). To accomplish this, first, a NaCl stock solution and water were added into an empty centrifuge tube, with volume ratio chosen to achieve the desired final overall salt concentration. This was followed by addition of stock solutions of polyanion, PSS, and of polycation, PDADMAC, respectively. The mixtures were vortexed for 30 seconds after each addition of water, polyanion stock solution, and polycation stock solution, respectively. Note that the mass of the polymer added can vary from the desired value by around -1.3% to 0.5% for PDADMAC and -3.5% to 5.7% for PSS because of limitations in pipetting, including some retention of polymer inside the pipette tips or extra drops clinging to the outside of tips. The final sample (typically 4.8 ml or 48 ml) was centrifuged for 15 minutes at 8,000g (Thermo Scientific, SORALL Legend X1R) after which the sample was left undisturbed for at least five days, long enough that the solution ceased to show any further changes in phase separation or appearance. After this, the supernatant phase was removed, leaving only the coacervate for rheological characterization and storage. Evaporation of water from the sample was minimized by sealing the tube with the parafilm tape. Shortly after the supernatant removed, a very thin layer of water would sometimes appear on top of the coacervate phase (usually in the samples with high salt concentration), which though visible is difficult to be removed by pipette due to its tiny amount.

C. Rheology

All rheology tests were performed on an Anton Paar MCR 702 rheometer using a stress-controlled motor at 20°C. Because of limited coacervate supply and to avoid high normal force, a fixture with diameter of 25mm (cone angle 2°) was usually used rather than ones with larger diameter. In addition, samples with PDADMAC MW = 400kDa, and PSS MW= 200kDa containing 2.8M and 3M NaCl, were even stiffer and could not be compressed to the desired gap even with the small-angle 25mm cone; for these, parallel plates with 25mm diameter were used. To minimize evaporation of water within PEC samples during long-time tests, the rheometer Peltier hood was employed and water was used to seal the solvent trap around the bottom plate. The temperature for all measurements was set at 20°C by the Peltier plate and hood setup. Strain sweeps were performed at 0.01, 10, 100 and 628 rad/s to identify the linear viscoelastic region (LVE) of the PEC. Long frequency sweeps were conducted at fixed strains (1%, discussed below) from 628 rad/s to 0.001 rad/s or oppositely, from low to high frequencies.



Scheme 1. Preparation process for PDADMAC/PSS/NaCl coacervates

III. Results and Discussion

A. Rheometer limitations

It is a challenge especially for low-viscosity liquids or soft solids to probe their stress with high resolution at either extremely low frequencies or at the highest frequencies allowed by the rheometer during oscillatory measurements. Thus, the low values of the modulus plateau, around 0.1Pa or even lower, sometimes reported in the low-frequency region of the oscillatory shear of coacervates [9][10][11][12], are of questionable accuracy. Theoretically, the lower limit of the modulus, measured in the cone and plate geometry can be calculated from equation (1) given the minimal oscillation torque of 0.5 nNm specified for the Anton Paar MCR702 rheometer. When the strain amplitude is set at 1% ($\gamma = 0.01$), the G_{lower} limit is computed to be around 0.016Pa for a cone and plate diameter of 25mm. In the high frequency region, the instrument inertia in the combined motor transducer (CMT) can lead to a measured frequency response of $G' \sim G'' \sim \omega^2$ for weakly elastic materials.

$$G_{\text{lower limit}} = \frac{2 \cdot \text{torque}}{\pi \cdot R^3 \cdot \gamma} \approx \frac{1.6 \times 10^{-4}}{\gamma} \text{ (Pa) if } R = 12.5\text{mm} \quad (1)$$

Although the torque limit and the system inertia can in principle be obtained from well-known formulas, other effects, such as surface-tension and other edge effects [16], calibrations, instrument vibrations, sample-loading effects (especially pertinent for soft solids), are difficult to be precisely predicted. These unclear sources of error lead to errors in moduli plateau that can be an order of magnitude greater than the theoretical torque limit. Thus, here we seek an empirical threshold for the polyelectrolyte solutions based on the experimental results of several reference fluids, including two low-viscosity liquids, namely water and a viscosity-standard oil (APS3, Anton Paar), a viscoelastic single-polyelectrolyte solution PSS (MW=2242kDa, PDI=1.19), and a PDMS reference viscoelastic fluid (AK 1 Million) (see SI). Because the limited volumes of coacervate samples restricted the rheometer fixtures to 25-mm diameter, all measurements on reference fluids presented in the main text were performed on the same small cone and plate at 1% strain amplitude using the CMT transducer, and therefore rheometer limitations established here only apply to this situation. Of course, higher accuracy and lower stress thresholds in frequency sweep tests can be achieved by using larger plates and/or higher strain amplitudes, as seen in Fig. S1 for measurements of air with a 50mm plate and in Fig. S2 for measurements of standard mineral oil, APS3, with dynamic strain amplitudes.

In FIG. 1a three repeat frequency sweeps of water yield G' data roughly following a “plateau” at values up to around 0.2 Pa, over frequencies ranging from 0.01 rad/s to 10 rad/s. These values are ascribable to the instrumental limitations since only noise is expected for G' measurements of water. Note that as the frequency increases above around 10 rad/s, power-law increases in G' and of G'' are found, (albeit with several G' data points dramatically lower) which are likely the result of inertia effects on the measurements in the CMT mode because the phase angles of those data points were reported as exactly 90° , which is the value the instrument reports when the angle exceeds 90° , as is expected for data dominated by inertial effects. In addition to the phase angle, the ratio of the sample torque over the electric torque was found to be less than 2%, mostly less than 1%, at high frequency, which also implies that inertia has a strong effect on these measurements. The oscillatory shear response of the viscosity-standard oil ($3\text{mPa}\cdot\text{s}$ at 20°), which should also have no elastic response within our rheometer limits, is found in FIG. 1b to be similar to that of water, with approximate plateau values G' up to around 0.1Pa. We note that measurements of this same fluid, in larger fixtures at higher amplitudes and a more precise transducer, produce a measurable viscoelastic response, given in FIG S2 in the SI, that is below the limits established in Figs. 1(a, b). Thus, the data points in FIG. 1 (a, b) are unreliable, as also shown by their lack of reproducibility in repeat runs. Hence, to exclude all noisy and unreliable data, we assign in FIG. 1 empirical thresholds for acceptable rheological measurements on the rheometer with CP25 fixtures. These limits are shown as a dashed horizontal line with magnitude 0.3Pa in the low ω region, and a diagonal line with power-law slope around 2.5 in the high ω region. These baselines are further confirmed by the single-component PSS polyelectrolyte solution, which is also observed to have a G' plateau of 0.01~0.1Pa in FIG. 1c, contradicting to

the literature observation [17], that shows no evidence of a G' plateau for measurements of a similar PSS solution using a large, 60mm diameter, plate. The remaining data points, which are above the threshold lines in FIG. 1c, which are mostly G'' points, are comparable to the literature results of single PSS solutions (see Figure 4c in the Ref 17), and therefore deemed reliable.

The fourth reference fluid, a standard viscoelastic PDMS solution (AK 1 Million, Wacker) yielded typical power-law slopes of G' and G'' in an oscillatory measurement at 1% and 10% strain on a parallel plate with 25mm diameter, as shown in Fig. S3, with G' reaching 0.03 Pa at 0.01rad/s below which data become noisy. This is below our cut-off of 0.3 Pa, and close to the theoretical limit of 0.016Pa at 1% strain, indicating that the practical threshold can be sensitive to the materials used, for example, the phase angle at low frequencies as well as the ambient vibrations and other factors.

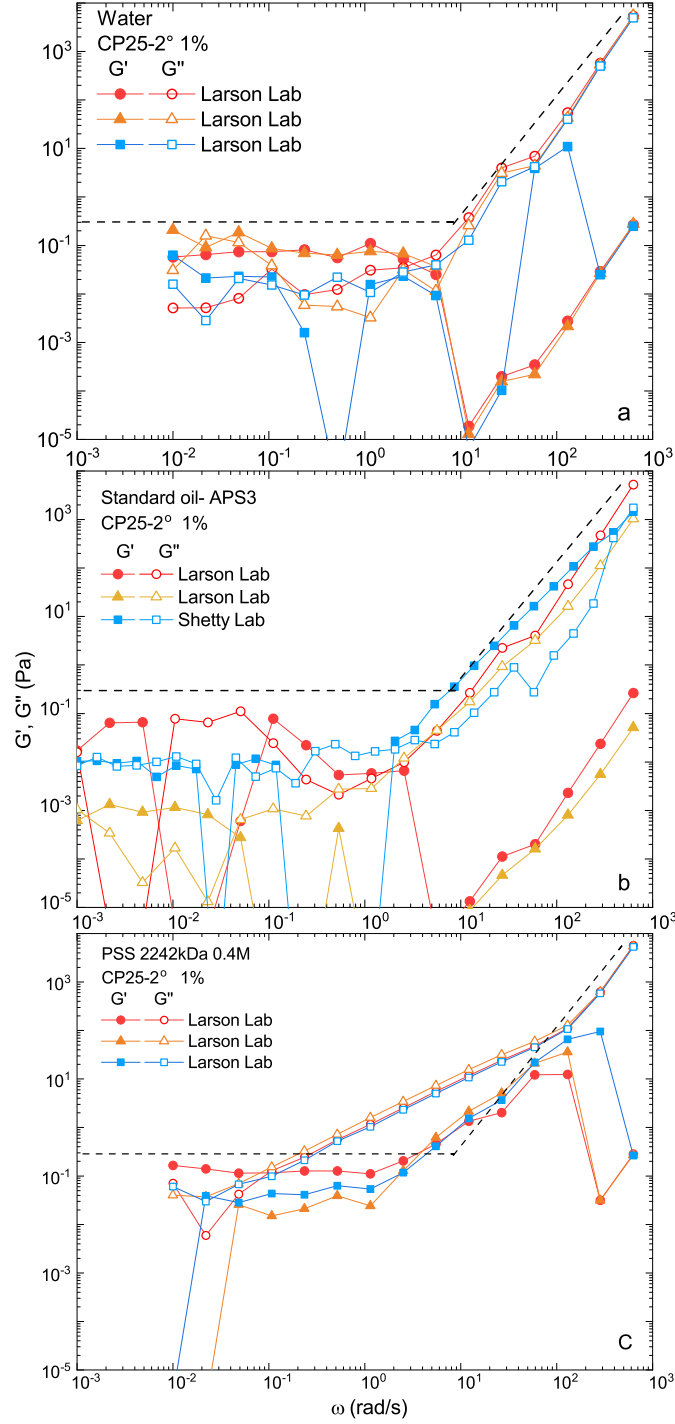


FIG. 1. Storage (G' , filled symbols) and loss (G'' , open symbols) moduli as functions of oscillation frequency obtained from repeat measurements of (a) water, (b) standard oil (tested in two laboratories), and (c) polystyrene sulfonate (PSS) solution at an amplitude of 1% strain on identical cone and plate rheometers (Anton Paar Inc) with 25mm fixtures in the Larson and Shetty Labs. Dashed lines are drawn empirically, and identically for all fluids, to exclude data points that are judged unreliable for the standard fluids studied.

B. Sample limitations

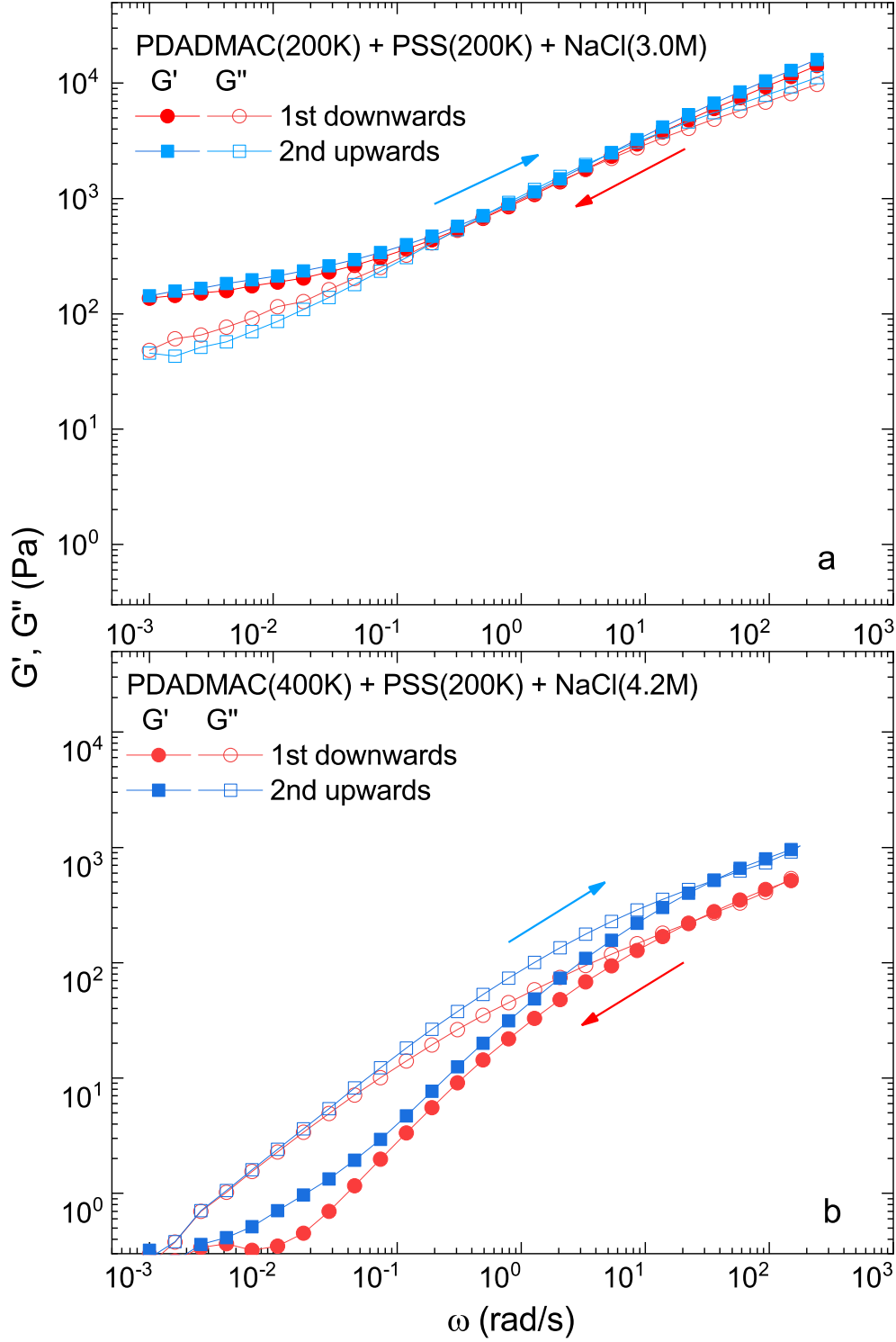


FIG. 2. Downward and upward frequency sweeps on coacervates of the same loading. Compositions are shown in the legends. Salt concentration refers to the overall concentration before phase separation. Data points below the threshold, 0.3Pa, are omitted for clarity.

In a frequency sweep, the rheological test time increases inversely with the lowest frequency attained. Around 4 hours are required for a sweep from 628rad/s to 0.001rad/s at three points per decade, and 6 hours at five points per decade. Such a measurement duration raises questions about sample constancy and test reproducibility. In FIG. 2, samples went through a downward frequency sweep and then an upward sweep with no waiting time between the two runs, taking 12 hours in total. We observe, in this test, that coacervates with less salt, such as the sample with 3M NaCl, were more reproducible than those with more salt, 4.2M, and are not as much affected by the frequency-sweep history. Note that salt concentrations mentioned in this paper refer to the designed salt concentration in the final mixtures before phase separation and the exact salt concentration in coacervate phase could differ from this [18][19]. We note that the more liquid-like coacervates, produced by a higher salt concentration seen in Fig. 2b, seem to be more prone to increasing modulus with the time, especially in the high-frequency region. Although we did not observe any direct evidence of it, we cannot rule out that this increased modulus could be the result of water evaporation due to the long time required for obtaining data at low frequencies. We did, however, use a hood to block evaporation and checked for slow changes in modulus by reproducing the frequency sweeps of some other samples shown in FIG. S4, and found only small changes for results between the first frequency sweep and the second repeated one.

FIG. 3 tests the reproducibility against aging of coacervate samples loaded and tested on different dates but identical testing conditions. Coacervates derived from mixtures with a total salt concentration of 3.4M report almost same rheological behaviors even after two-month storage of the sample, shown in FIG. 3 (a) and (c), while samples prepared with the highest overall salt concentration, 4.2M, exhibited a considerable increase in moduli and change in the shape of the rheological curves. This time sensitivity is probably affected by the hydration level inside the coacervates. Long-time storage could lead either to slow phase equilibrium or, more likely, to some evaporation of water, which can be detected by increased moduli. Thus, there is incentive to finish rheological measurements quickly after sample preparation to minimize changes in hydration level during experiments. Note that in Fig. 2b and Fig. 3d, there are storage moduli showing a short plateau window around the threshold, 0.3Pa, at frequencies lower than 0.05rad/s. These plateaus are doubtful and probably experimental artifacts since they are close to the noise level and thus not taken as low-frequency plateaus. Apart from the above caveats, our investigation of batch-to-batch and lab-to-lab reproducibility of coacervates, seen in FIG. 4, reveal quite repeatable measurements not only for liquid-like coacervates but also for gel-like ones, which further demonstrates the reasonable accuracy and reproducibility of our experiments.

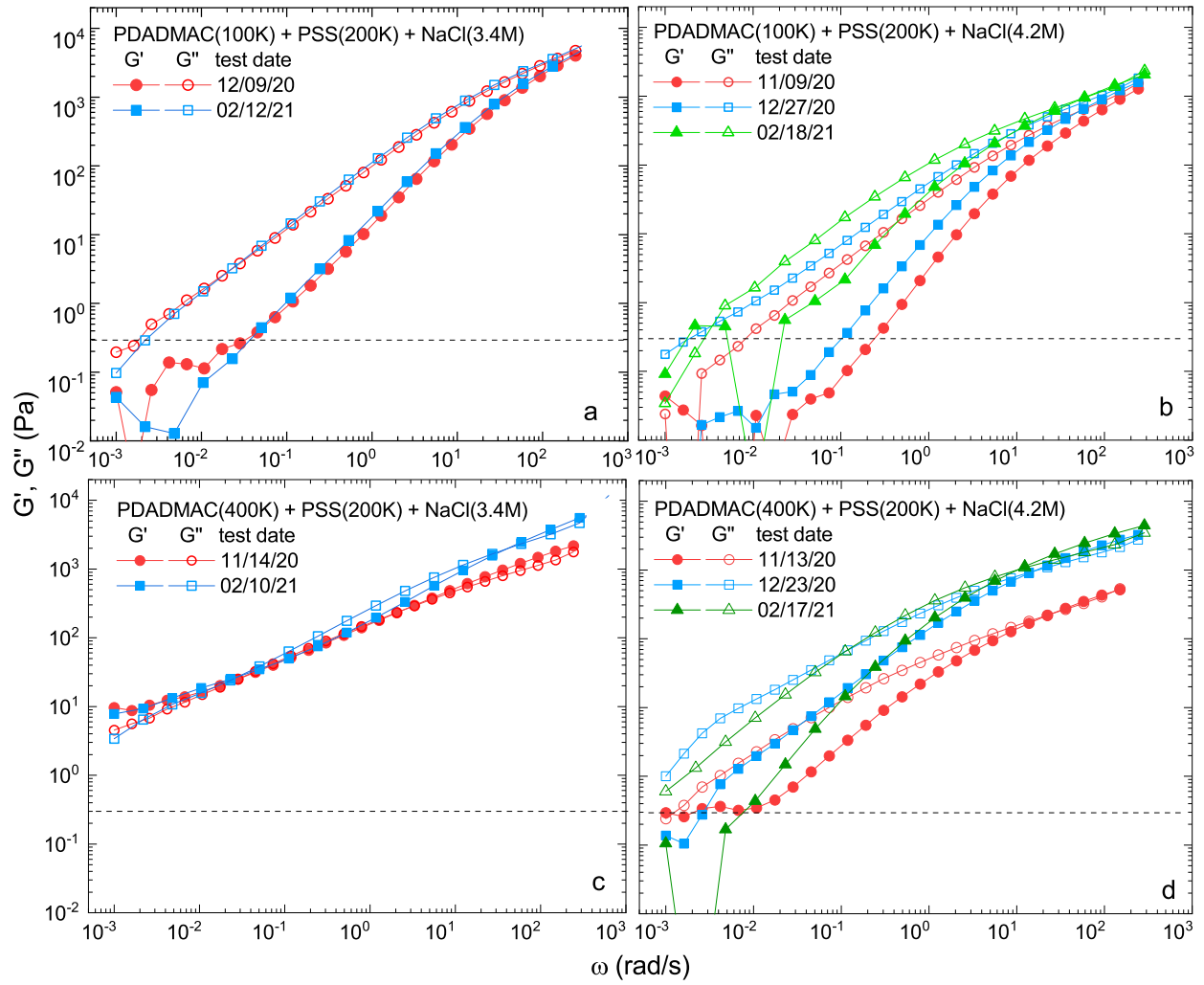


FIG. 3. Frequency sweep curves of PDADMAC/PSS complexes on different dates with the same PSS chain length (200kDa) but different molecular weight of PDADMAC: (a, b) 100kDa and (c, d) 400kDa. The overall salt concentrations of samples are given in the legend. Any data below the dash line (0.3Pa) is not reliable.

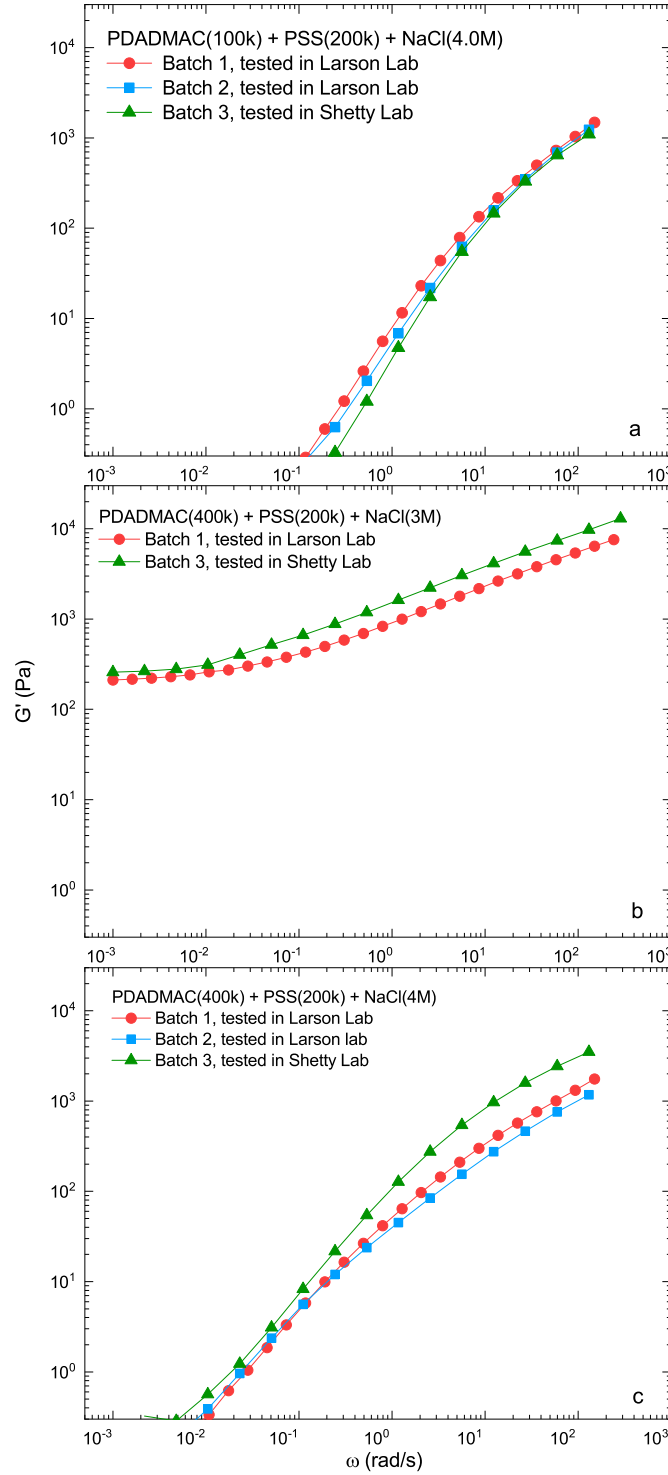


FIG. 4. Batch-to-batch linear viscoelastic reproducibility of coacervates measured in two different laboratories. Samples from Batch 2 and 3 were prepared through the same stock solutions at the same time, while batch 1 was from earlier stock solutions and prepared six months earlier. Data points below the threshold for reliability, 0.3Pa, are omitted.

C. Region of linear viscoelasticity of coacervates

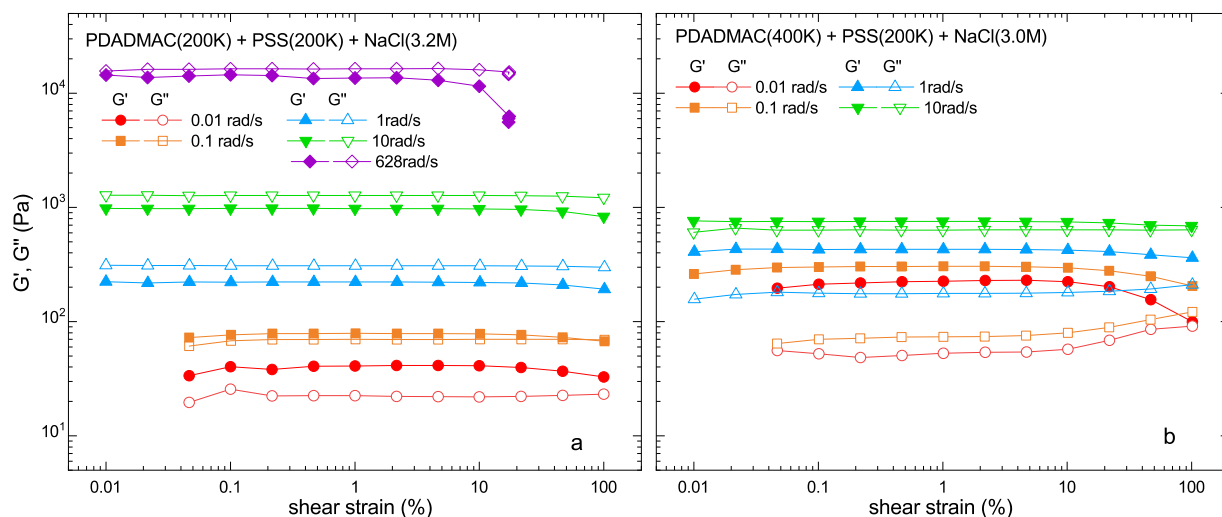


FIG. 5. Strain sweeps from 0.01% to 100% of polyelectrolyte coacervates at frequencies of 0.01, 0.1, 1, 10, and 628rad/s. Sample compositions are given in the legends.

The linear rheological values of G' and G'' in oscillatory shearing can only be obtained within the “small-strain” limit, which can be unusually small for polymer gels [20]. The linear viscoelastic region (LVE) is often confirmed by performing strain sweeps at various frequencies, e.g., 1rad/s or 10rad/s. In most cases, the linear region obtained from one or two frequencies is assumed to apply across the whole range of frequencies. However, more caution is required for samples showing gel-like behavior over some frequency range. In FIG. 5a, it is seen that at frequencies lower than 10 rad/s, the linear region reaches up to 20%, but fails at 10% strain at 628rad/s. This is consistent with the typical behavior of viscoelastic materials, which show a smaller linear region at higher frequencies. Interestingly, FIG. 5b exhibits the opposite behavior in that a smaller range of linear behavior is observed at low frequencies, namely 0.01 and 0.1 rad/s, for which the moduli drop quickly when the strain is increased beyond 10%. Since the strain sensitivity not only limits the linear viscoelastic region, but may also indicate the possibility of strain-induced “damage” or long-lasting changes to coacervate structure, we choose 1% strain as a “safe” amplitude for all frequency sweep measurements discussed below. Such a small strain amplitude and plate diameter, however, limits the accuracy of instruments, especially at low frequencies, and helps set the threshold of 0.3Pa minimum modulus for our reported data.

D. Effects of salt concentration on polyelectrolyte complexes

In polyelectrolyte coacervates, salt is commonly treated as a “plasticizer” since it can increase hydration level and screen the electrostatic interactions between ion groups. Changing salt concentrations can shift the G' and G'' curves, while leaving their shape unaffected [7]. Thus, the principle of “time-salt superposition” has been used in the literature to shift curves at high salt concentration to lower frequencies and thereby expand the frequency range of the rheological data, based on the assumption that salt does not change the local relaxation mechanisms, but only adjusts their speed. Time-salt superposition has been verified in multiple polyelectrolyte systems [8][21].

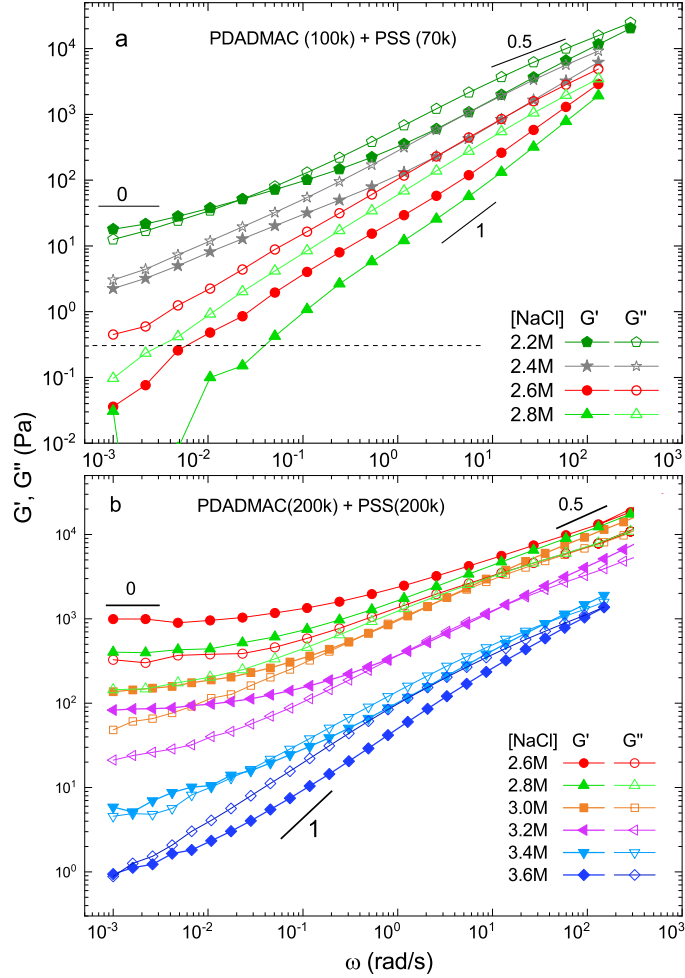


FIG. 6. Linear viscoelastic curves for PDADMAC/PSS/NaCl coacervates of different molecular weights and salt concentrations, as given in the legends. In (a) the dashed line represents the empirical baseline 0.3Pa, below which the data are not reliable.

However, it has been reported recently that some frequency dependencies cannot be time-salt superposed, especially in the low-frequency region [14]. To study rheological behavior at longer timescales in the coacervate system (PDADMAC/PSS/NaCl), we extend oscillatory shear to a lower frequency than typical, namely down to $\omega = 0.001 \text{ rad/s}$, and avoid time-salt superposition. We thereby find in FIG. 6 that differences of the shape of the curves become larger at low frequencies, developing a flat region of G' for high molecular weights and lower salt concentrations in FIG. 6b. With salt concentration decreasing from 3.6M to 2.6M in FIG. 6b, the magnitudes of both G' and G'' increase, and G' is above G'' at all frequencies at the lowest salt concentration, 2.6M. The most notable feature in FIG. 6b is that coacervates with salt concentrations of 2.6M, 2.8M, 3.0M, and 3.2M show high storage moduli, ranging from 1000Pa to 100Pa, with relatively low sensitivity to frequency, across two decades of ω from 0.1rad/s to 0.001rad/s. The appearance of a near-plateau at the lowest frequencies may indicate that the coacervate has changed to a gel-like material. However, to avoid possibly falsely ascribing such behavior to the presence of a “plateau”, we will require any low-frequency plateau we take as “real” to display relatively constant G' values exceeding our prescribed noise level (0.3 Pa) for at least one decade of frequency. At higher salt concentrations, 3.4M and 3.6M, in FIG. 6b, the coacervate

exhibits no clear plateau, but instead an intermediate behavior between liquid-like and solid-like, with $G' \approx G'' \sim \omega^{0.5}$ over most of the frequency range, similar to what Ali & Prabhu reported [14] and similar to other observed gel transitions [22][23]. Here, it is possible that the curve with a slope of 0.5 represents a critical gel point, below which (at higher salt concentration) the coacervates are in the pre-gel regime, and above which (i.e., for less salt) samples are in solid-like gel state. However, the data above and below the transition cannot be separately superposed into two “master curves,” one for the liquid and the other for the gel, as can sometimes be done for other gelling systems. We conclude from this that salt not only changes the local rate of chain motion, allowing for shape-independent shifting of G' and G'' curves, but can also produce a gradual structural transition from a liquid-like solution to a solid-like network as salt concentration decreases.

For the same PE system but for shorter chain length, shown in FIG. 6a, we did not observe a clear G' plateau at any frequency. However, the 2.2M sample presents fairly flat scaling, $G' \sim \omega^{0.2}$ as well as $G' > G''$, at low frequencies. It may be possible that a plateau region can be attained if ω could be extended to low enough values, but these are impractical to reach within the time scales allowed for our experiments.

E. Effects of chain length on low-frequency plateau

FIG. 6 indicates that polyelectrolyte chain lengths, as well as salt concentration, influences the transition to the solid gel state. To examine this in more detail, we prepared samples with different polycation molecular weights, namely 100kDa, 200kDa and 400kDa, and polyanion MWs of 70kDa and 200kDa, leading to six different combinations of the molecular weight of polyanion and polycation. FIG. 7(a, d) shows that plateaus are only definite when the chain length of PDADMAC is higher than 100kDa, namely 200kDa or 400kDa, no matter the chain length of PSS. But FIG. 7(b, c) shows that the plateaus do not disappear when the PSS MW is lower than 100kDa, namely 70kDa. This seems to indicate that the appearance of a gel-like structure is more dependent on the chain length of the polycation rather than polyanion for this system. Interestingly, the magnitude of the G' at plateau is much more affected by the chain length of the polyanion, PSS. This is shown in FIG. 7 (b) and (c), where an increase in PDADMAC MW from 200kDa to 400kDa at a fixed salt concentration of 2.8M (green triangle symbols) or 3.0 M (orange square symbols) causes less than a doubling of the G' value, while in FIG. 7 (b) and (e), at 2.6M NaCl, a five-fold increase in modulus occurs, from 200Pa to around 1000Pa, upon increase in PSS MW from 70kDa to 200kDa. This may indicate that the plateau value, once it exists, is more sensitive to PSS than to PDADMAC MW in this system.

The above observation does not seem to be general, and the opposite influence could be observed if different combinations of polyelectrolytes are chosen. For example, Spruijt and coworkers [8] found that the length of their polycation, PDMAEMA, affected the viscoelastic response more strongly than did their polyanion, while we showed that the length of our polyanion, PSS, has a significant effect on the value of modulus.

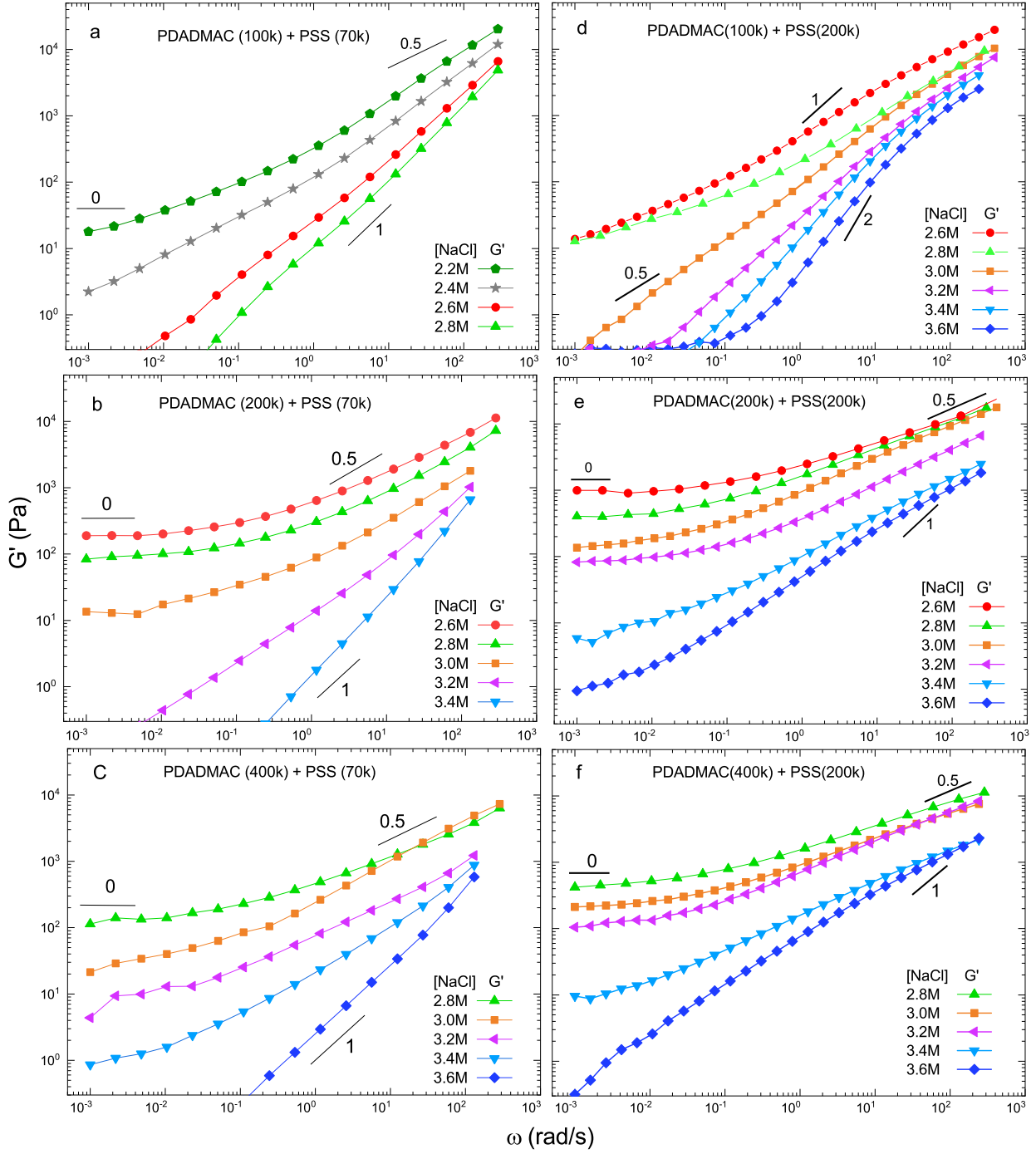


FIG. 7. Storage moduli for six polyelectrolyte complexes composed of three chain lengths of PDADMAC with (a, d) MW=100kDa, (b, e) MW=200kDa, and (c, f) MW=400kDa, and two chain lengths of PSS with (a-c) MW=70kDa and (d-f) MW=200kDa for various NaCl concentrations, given in the legends. Storage and loss moduli below the reliability threshold of 0.3Pa were omitted.

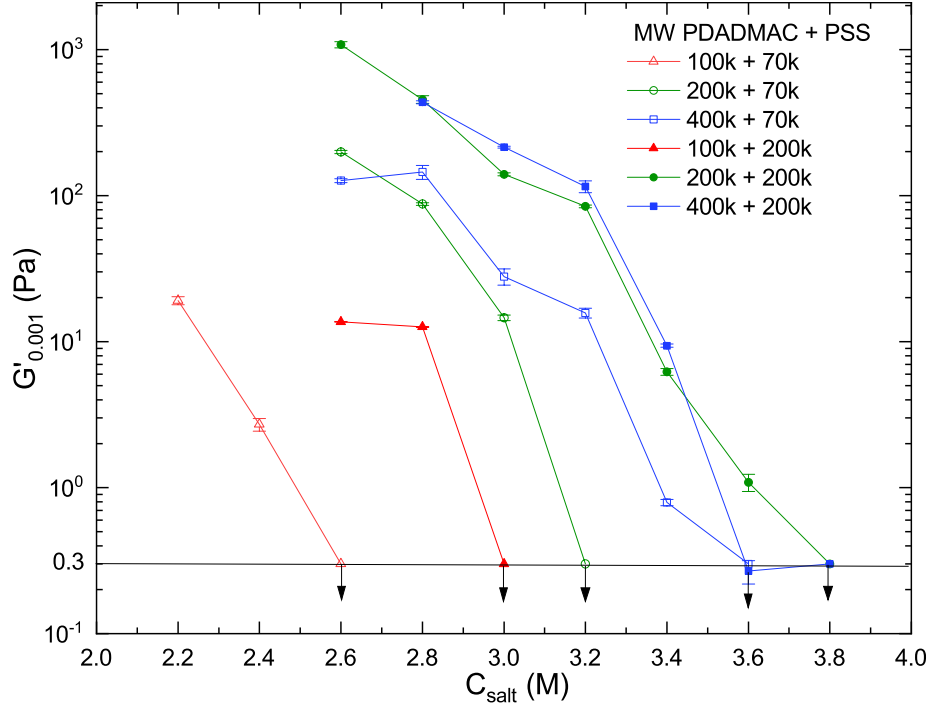


FIG. 8. Comparison of storage moduli at the lowest frequency of 0.001rad/s as function of salt concentration for six sets of coacervates of different chain lengths, shown in the legend. The cutoff G' is 0.3Pa as discussed above, and so data below this threshold were indicated by a data point on this line and a downward-pointing arrow. Each error bar given was calculated from the repeat runs of long-time frequency sweep of the same loading within 12 hours. Some error bars are covered by the symbols.

Longer polyelectrolyte chain lengths slow the relaxation of the coacervates, while more salt lubricates and accelerates chain dynamics. These effects on chain mobility have been well established in previous work [24][25]. The effect of salt concentration can often be quantified by time-salt superposition [6], which produces primarily a shift of the G' and G'' curves along the frequency axis. However, we also find that both salt and molecular weight affect the presence and magnitude of a low-frequency plateau modulus, an effect which does not follow time-salt superposition. The effects of salt concentration and chain lengths on the storage moduli at low frequency in our work are summarized in FIG. 8. The coacervate composed of 70kDa PSS and 100kDa PDADMAC at 2.2M, represented by the left-most red open triangle in FIG. 8, has a modulus of around 20Pa, that is similar to that of a coacervate of 200kDa PSS and 100kDa PDADMAC at 2.6M, which is given by the left-most red filled triangle. Both coacervates composed of 200kDa PDADMAC, but with PSS of 70kDa at 2.8M salt (an open green circle) and of 200kDa PSS at 3.2M (a filled green circle), have low-frequency plateau moduli of 100Pa. Note in FIG. 8 that the data represented by filled circles/squares can be shifted toward lower salt region to superpose roughly with the data with open circles/squares, especially for data points with G' above 10 Pa. It would be worth investigating that whether a model could predict these interesting dependencies of low-frequency modulus plateau on PE chain lengths and salt concentration and identity.

F. Literature values of low frequency plateau modulus

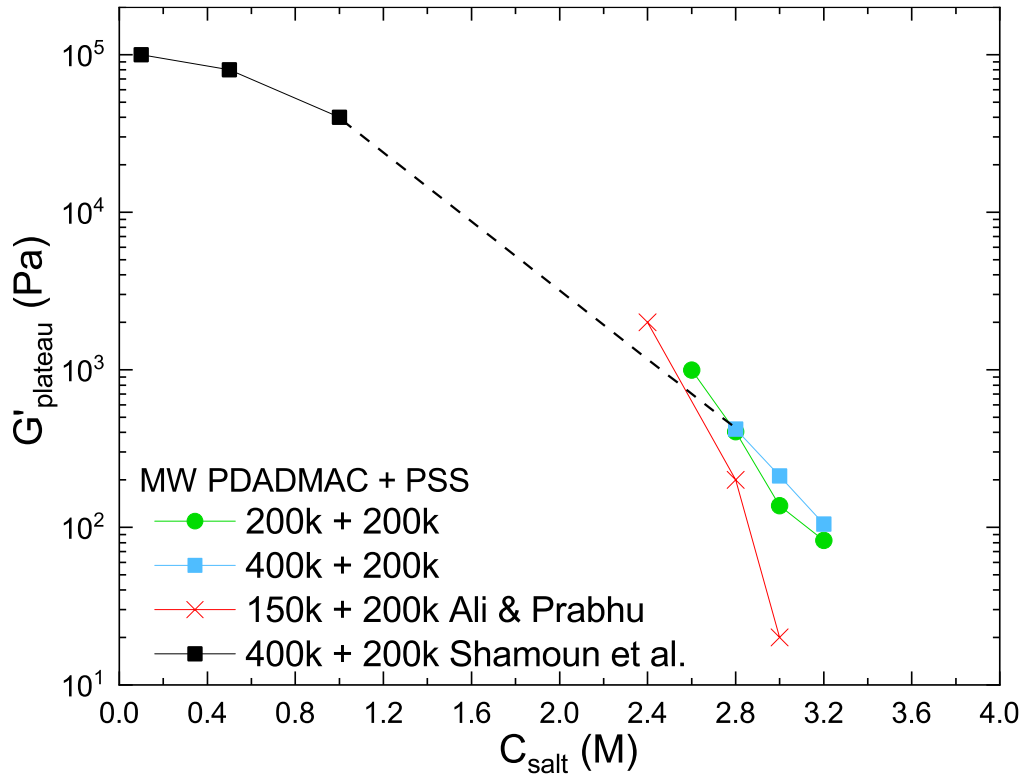


FIG. 9. Comparison of G' low-frequency plateau for PDADMAC/PSS/NaCl coacervate complexes as function of salt concentration. Literature data is extracted from Ali & Prabhu [14] and Shamoun et al. 2012 [13]. Molecular weights shown in the legend represent the MW of PDADMAC and PSS, respectively.

For coacervates prepared from PDADMAC, PSS and NaCl, Ali and Prabhu [14] previously reported a low-frequency plateau for G' at frequencies as low as 0.01 rad/s, obtained through time-temperature superposition. FIG. 9 shows that their samples with 150 kDa PDADMAC have slightly lower modulus than ours with 200 kDa PDADMAC. The data for three chain lengths of PDADMAC, ranging from 150 kDa to 400 kDa, show no large increase in plateau modulus. Note that, in our experiments, the low-frequency plateau did not appear for samples with 100 kDa PDADMAC over the range of salt concentration considered. It is possible, therefore, that there is a critical chain length of PDADMAC between 100 kDa and 150 kDa for forming a gel-like structure at long timescale. A much larger plateau was found by Schlenoff group [26], for similar samples to ours, but prepared by adding smaller concentrations of salt (less than 1 M) into already-prepared precipitates, rather than through phase separation, as we have done. Despite this difference in preparation procedure, we find that a reasonable extrapolation of their data to higher salts, leads to moduli consistent with our data set (PDADMAC with 400 kDa).

This comparison with literature data reveals that the appearance of a low-frequency plateau is a common and consistent feature of this strong PE system (PDADMAC/PSS). It may be possible

that many other pairs of strong polyelectrolytes might reveal a gel-like response at low frequencies if they are studied at high enough molecular weights and low enough salt concentrations. A recent scaling theory by Rubinstein and coworkers [27] attributes the transition from liquid-like to solid-like behavior to an increase in binding free energy between oppositely charged monomers from less than, to greater than, ~ 1 k_BT. When the solid forms, however, its magnitude is estimated to be of order the density of charged monomers, a value much too high to be consistent with the values we find at high salt concentration.

Theories, simulations [28], experimental results [29] for gel formation in neutral associating polymers [30] might provide clues for developing a predictive theory for gel formation in polyelectrolyte coacervates. The relationship between a low-frequency plateau modulus and the structure and dynamics of associating polymers, including charged polymers, was explored recently by Zhang et al. [31]. Key ideas explored in this work include: 1) the relationship between plateau modulus $G_0 = \rho RT/M_s$ and the density of strongly associating groups, quantified by the average molecular weight M_s of a strand between associating groups, with ρ the mass density of polymer; 2) the transition of charged polymers from a “polyelectrolyte regime” to an “ionomer regime” as determined by average ion spacing along the chain and the product of dielectric constant and temperature with lower values of each favoring the “ionomer regime,” in which opposite charges not only pair, but form clusters of multiple positive and negative ions; 3) the existence of a “percolation regime” in which roughly one strong binding site is found on each chain, and the modulus can be arbitrarily small and sensitive to density of binding sites. The formula $G_0 = \rho RT/M_s$ applied to coacervates with typical polymer volume fraction of ~ 0.3 , implies that polymers with $M_s \sim 200,000$ Da would have a modulus of around 5×10^3 Pa. This implies that many of our coacervates, especially at higher salt concentration, have fewer than one network-forming bonding site per polymer, obviously far less than the number of charges per chain. We also find that the presence and magnitude of the plateau modulus depends not only on salt concentration, but also on chain length, suggesting that the spacing between the strong binding sites is comparable to, or larger than the chain length, so that shorter chains are less likely to form a percolating network of bound chains than are longer chains. Not only is the number of ion pairs likely to be present in coacervates too large to explain the low-frequency modulus, but their lifetimes are likely too short, based on estimates of ion pair lifetimes by Schlenoff and coworker [26], among others [6][8]. In addition, ion-pairing lifetime and its dependence on salt concentration is the basis for explaining time-salt superposition, and the height of the plateau modulus depends on salt concentration and therefore does not obey time-salt superposition.

For these reasons, the low-frequency modulus is likely controlled not by simple ion pairs, but by longer-live aggregates of multiple monomers of both positive and negative charge. Such aggregates are present in ionomers [31], and become more likely when the dielectric constant decreases, as is likely to happen locally within a coacervate with lower amounts of salt and less water of hydration. The transition to the “ionomeric regime” is predicted by Zhang et al. to occur at charge spacings and dielectric constants typical of coacervates, especially if one allows for a broad transition region from the “polyelectrolyte” to the “ionomer” regime as envisaged by Colby and coworkers (see Fig. 3 of Zhang et al.) [31]. A picture that might explain that plateau modulus is therefore one in which, in addition to abundant ion pairs, there are aggregates of charged monomers, held together part by a locally high polymer concentration that lowers the local dielectric constant, supporting a locally “ionomeric” environment within the coacervate. The

aggregates are likely to be of various sizes and lifetimes, and thus one expects a gradual approach to a plateau as frequency decreases, as aggregates of a range of sizes and lifetimes contribute to the modulus. This is consistent with the gradual broadening of the relaxation spectrum of a coacervate, as salt concentration decreases, eventually leading to a low-frequency plateau, as indicated in FIG. 7. Clear fluid-like terminal regimes are largely absent from our data, which instead show intermediate power laws between “liquid-like” and “solid-like” order, tending gradually towards more “solid-like” behavior as the salt concentration decreases. Thus, we picture coacervates that either have a low-frequency G' plateau or have intermediate power law dependences of G' and G'' on frequency as heterogeneous phases with patches of “ionomer-like” material, with low dielectric constant and multiple aggregated charged monomers, with long lifetimes, creating a percolating or near-percolating network structure. We note that this explanation of the low-frequency low modulus of coacervates is consistent with earlier suggestions of a percolated network of chains or domains by Bohidar et al. [12] for coacervates formed by mixtures of charged proteins and polyelectrolytes.

IV. Conclusion

The rheological behaviors of polyelectrolyte complexes in the low frequency region were revealed more thoroughly and decisively than in previous work, through frequency sweeps down to low frequencies at small strain amplitude, for all six combinations of three commercially available poly (diallyl dimethyl ammonium chloride) (PDADMAC) samples with two poly (sodium 4-styrenesulfonate) (PSS) samples. To obtain reliable data, we determined the limits on experimental accuracy and reproducibility due to rheometer sensitivity, and sample stability against evaporation, aging, and rheometer loading, through repeat tests using two different rheometers, and through measurements on reference standards, yielding clear bounds on acceptable data. We found that coacervates at the highest salt concentrations (close to 4 M) have poor reproducibility, leading to exclusion of these samples from our reported data sets. The formation of a low-frequency plateau and its magnitude are found to be highly sensitive to salt concentration, consistent with previous work. Novel to our work is the finding that it is also sensitive to polyelectrolyte molecular weight, with more rapid increase in its magnitude with increasing length of the polyanion, PSS than of the polycation, PDADMAC. Trend lines of the dependences on salt concentration and chain length are assembled from our data and relevant literature. Why both salt and chain length can, under some circumstances, not only shift the rate of chain motion, but also quench long-range motion into a gel-like response, is a mystery that needs resolution, and a theory to reliably predict it. We suggest that a transition towards a network of “ionomer-like” aggregates might provide a fruitful starting point.

Supplementary Material

See supplementary material for the complete rheological measurements of the air, the standard oil (APS3), the standard PDMS solution (AK 1 Million), and downward and upward frequency sweeps on polyelectrolyte coacervates.

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