

Electrochemical Determination of the Glass Transition Temperature of Thin Polyelectrolyte Brushes at Solid–Liquid Interfaces by Impedance Spectroscopy

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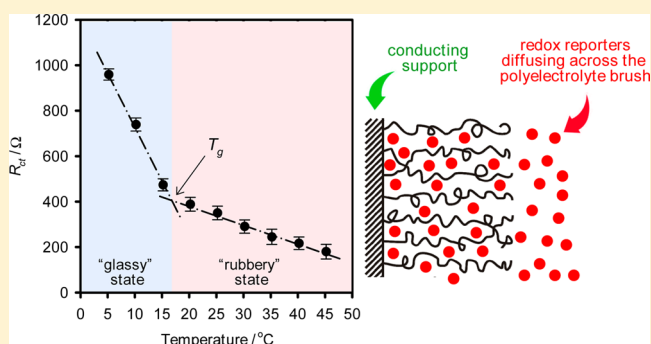
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Supporting Information

ABSTRACT: Devising strategies to assess the glass transition temperature (T_g) of polyelectrolyte assemblies at solid–electrolyte interfaces is very important to understand and rationalize the temperature-dependent behavior of polyelectrolyte films in a wide range of settings. Despite the evolving perception of the importance of measuring T_g under aqueous conditions in thin film configurations, its straightforward measurement poses a challenging situation that still remains elusive in polymer and materials science. Here, we describe a new method based on electrochemical impedance spectroscopy (EIS) to estimate the glass transition temperature of planar polyelectrolyte brushes at solid–liquid interfaces. To measure T_g , the charge transfer resistance (R_{ct}) of a redox probe diffusing through the polyelectrolyte brush was measured, and the temperature corresponding to the discontinuous change in R_{ct} was identified as T_g . Furthermore, we demonstrate that impedance measurements not only facilitate the estimation of T_g but also enable a reliable evaluation of the transport properties of the polymeric interface, i.e., determination of diffusion coefficients, close to the thermal transition. We consider that this approach bridges the gap between electrochemistry and the traditional tools used in polymer science and offers new opportunities to characterize the thermal behavior of complex polymeric interfaces and macromolecular assemblies.



Knowledge of the influence of temperature on the physical properties of thin polymer films as well as appearance of thermal transitions in surface-grafted macromolecular systems are key aspects that play major roles in many technological applications.¹ For many years, now, and particularly within the past decade, special interest has been paid to the estimation of the glass transition temperature (T_g) of thin polymer films, i.e., the temperature at which the polymer film experiences a transition from a glassy to a rubbery state.^{2,3} In most of the cases, determination of T_g in thin film configurations is much more difficult to accomplish than in typical bulk samples. The main reason for that is the reduction in signal strength because less material is being probed, and concomitantly, this effect could also have an impact in the slopes of the curves relating a property being measured versus the temperature that characterizes the glass and melt regions.⁴ Nevertheless, different groups developed different successful strategies based on ellipsometry,⁵ surface plasmon resonance spectroscopy,⁶ X-ray reflectivity,⁷ or fluorescence spectroscopy⁸ to achieve such a goal. More recently, there has been great emphasis on studying the thermal behavior and estimating T_g of polyelectrolyte-based thin films

in aqueous environments.⁹ Interfacial architectures based on polyelectrolytes, like layer-by-layer assemblies or polyelectrolyte brushes, have become versatile materials for the design and fabrication of a broad variety of smart functional devices including self-assembled capsules, membranes, sensors, or drug delivery systems.¹⁰ In all of these applications, the same experimental scenario takes place: polymeric assemblies are in contact with a liquid phase. As mentioned above, a number of techniques and protocols are available to determine T_g in thin films at the gas–solid interface; however, the choice is much more limited for estimating T_g in thin films fully immersed in electrolyte solutions. Therefore, it is crucial to develop straightforward but reliable techniques that enable an in situ estimation of T_g of polyelectrolyte assemblies without drawing upon complex experimental setups, specific sample preparation, or even arguable assumptions for data analysis. In this context, electrochemical (Faradaic) impedance spectroscopy (EIS) is

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rapidly evolving as a very versatile electrochemical technique fully compatible with the in situ characterization of polyelectrolyte brushes grafted on solid surfaces.¹¹ This technique has facilitated the accurate electronic transduction¹² of a series of stimuli-triggered responses in different polymer brushes.¹³ For example, Minko, Katz, and co-workers explored the switchable properties of mixed polymer brushes arising from morphological transitions in the polymer brush layer using EIS under different conditions in liquid environments.¹⁴ So far, temperature-dependent EIS studies on polymer brushes have been exclusively circumscribed to the characterization of the switchable gating properties of polymer brushes bearing thermoresponsive monomers, e.g., isopropylacrylamide (NIPAM).¹⁵ In this work, we describe for the first time the use of EIS as an electrochemical method to estimate the glass transition temperature of polyelectrolyte brushes in aqueous electrolyte environments. We show the capabilities of EIS to demonstrate that ion-paired polycationic thin polymer brushes display a well-defined T_g near room temperature. Although solvent-driven glass transition was reported previously for polyelectrolyte brushes,¹⁶ a temperature-driven glass transition like the one reported here was not and this could have immediate implications in their molecular transport properties.

Cationic poly(2-(methacryloyloxy)ethyltrimethylammonium perchlorate) (PMETAP) brushes were synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP) of the monomer 2 (methacryloyloxy)ethyltrimethylammonium followed by counterion exchange in the presence of 0.1 M NaClO₄ (Figure 1).¹⁷ Polymer brushes were then characterized by in situ ellipsometry to estimate the thickness of the PMETAP brushes (see Supporting Information for further details).

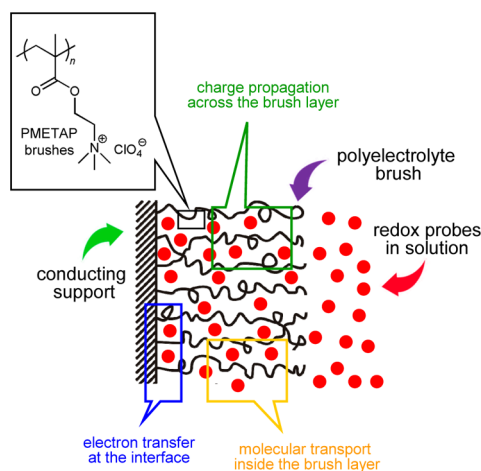


Figure 1. Schematic representation of the different charge- and mass-transport processes taking place in the system constituted of a gold substrate modified with PMETAP brushes in a solution containing redox probes. See the text for the full description of the transport processes prevailing under our experimental conditions.

Thereafter, we carried out the EIS characterization of PMETAP brushes in an electrolyte solution 0.1 M NaClO₄ containing a 1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture (redox probes) at different temperatures. EIS is a versatile method for probing the features of surface-modified conducting supports.¹⁸ A small-amplitude perturbing sinusoidal voltage signal is applied to the electrode surface, and the resulting

current response is measured. This particular feature renders EIS a very sensitive technique to monitor subtle changes in electrical properties of solid–liquid interfaces.¹⁹ Moreover, EIS probes not exclusively the solid–liquid interface but also bulk processes, like mass transfer, that govern the value of the surface concentration of the electroactive molecules. In the studied system, the diffusion layer spans the whole brush thickness. Figure 2 shows the impedance spectra of PMETAP

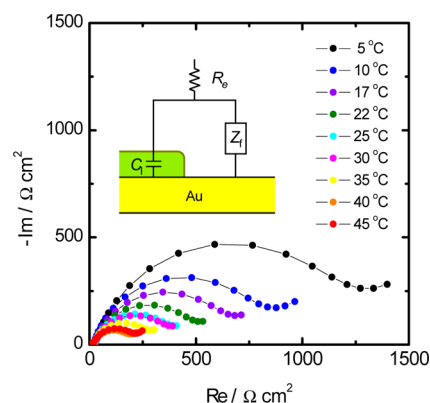


Figure 2. Nyquist plot (Z_{im} vs Z_{Re}) for the Faradaic impedance measurements performed at different temperatures in the presence of 1×10^{-3} M Fe(CN)₆^{3-/4-} + 0.1 M NaClO₄ at a Au electrode modified with poly(2(methacryloyloxy)ethyltrimethyl ammonium perchlorate) (PMETAP) brushes. Measuring frequency range 10^5 – 10^{-1} Hz. The inset displays the theoretical equivalent circuit used to fit the experimental data. R_e : electrolyte resistance; C_i : interfacial capacitance resulting from a distributed impedance element CPE; Z_f : faradaic impedance.

brushes measured at different temperatures. These plots are presented in the form of complex plane graphs (the so-called Nyquist plots), in which the semicircle diameter corresponds to the electron transfer resistance (R_{ct}) of the redox reporters, i.e., Fe(CN)₆^{3-/4-}, at the electrode surface. In order to derive accurate values of R_{ct} from the experimental spectra, the data were fitted to a theoretical equivalent circuit (inset in Figure 2). For the high frequency data in Figure 2, the faradaic impedance $Z_f = R_{ct}$. A plot displaying the electron transfer resistance versus temperature is presented in Figure 3. As expected, electron transfer is an activated process and, consequently, R_{ct} decreases upon increasing temperature. However, EIS is able to detect within the experimental temperature domain two well-defined regions that are associated, in principle, to two different activation energies. Straight lines drawn in Figure 3 are not intended as an indication of strict linear behavior but as a clarification of the bounds of each region. The R_{ct} vs T curve displays a kink, which is attributed to the thermally induced glass transition. As is discussed below, the changes in activation energies for the diffusion and electron transfer processes measured after lowering the temperature below a certain critical value are not arbitrarily linked here with a glassy–rubbery state transition, but rather, this event appears as the only plausible interpretation of the experimental results. It is also important to mention here that similar experiments performed in the absence of polymer brushes, i.e., gold electrodes modified with ATRP initiator-terminated self-assembled monolayers, revealed plots with a single value for the activation energy (see Supporting Information for details). Hence, the presence of a breakpoint in Figure 3 leading to temperature domains with

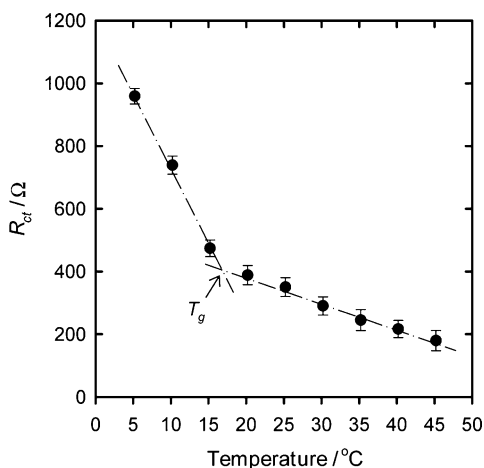


Figure 3. Representation of the charge transfer resistance (R_{ct}) derived from EIS measurements plotted in Figure 2 as a function of temperature (T).

different activation energies is a clear indication that the thermal transition occurring in the brush layer is responsible for altering charge transfer resistance values. Charge transfer dynamics at electrode surfaces chemically modified with polymeric building blocks is strongly influenced by structural changes in the macromolecular array and provides an assessment of physical changes in the polymer layer.²⁰ The different slopes of the straight lines in the R_{ct} vs T plot reveal the transition between glassy and rubbery states. Traditionally, the physical changes occurring in the polymer film at T_g have been explained on the basis of free volume and cooperative motion of the macromolecular assembly.²¹ In our case, electron transfer of redox probes embedded in a “glassy” polymer brush represents a process with high activation energy. This fact might be ascribed to the reduced segmental motion of polymer chains and free volume at the electrode surface that render the electron transfer a costly process.²²

In the most general case, the electroactivity in polyelectrolyte films hosting redox counterions relies not only on the charge transfer of the redox species at the electrode surface but also on the movement of electrons in a diffusive manner among the neighboring redox centers (Figure 1). For instance, the redox process is coupled to the incorporation of ions and solvent molecules into the film in which swelling or shrinkage of the polymer brush can take place.²⁰ Thus, the electrochemical process with the polyelectrolyte brush in the presence of the redox probes can be, under certain experimental conditions, rather complicated, particularly due to the possible interaction between the $\text{Fe}(\text{CN})_6^{3-/4-}$ anions and the brush chains. $\text{Fe}(\text{CN})_6^{3-}$, once mixed with the cationic polyelectrolyte brushes, would preferentially replace and release the monovalent counteranion perchlorate from the brush film and introduce ionic cross-linking of the brush chains.²³ However, in our experiments, the concentration of perchlorate anion is 100 times that of each redox species, what in principle reduces substantially the occurrence of this event. In principle, the charge transport mechanism might involve either movement of the electroactive ions by diffusion or hopping/tunneling of electrons from one redox site to the next at fixed positions in the polymer chain.²⁴ Interestingly, Huck and co-workers²⁵ demonstrated that in $[\text{Fe}(\text{CN})_6]^{3-}$ -coordinated PMETAC brushes ion diffusion rather than electron hopping is the charge transport mechanism taking place even for comparable

concentrations of the redox species and the counterion. Hence, in the case of PMETAP brushes upon increasing temperature above T_g , the reorganization and higher mobility of grafted chains facilitates not only the movement of redox probes to close proximity of the electrode surface but also the charge propagation across the film. Hence, this electron transfer process is energetically more favorable than a similar one occurring below T_g . Differences between both thermal regimes, glassy and rubbery, are clearly manifested by a well-defined variation in activation energy for the electron transfer process of the redox probe. Figure 4 shows a plot of $\ln(T/R_{ct})$ versus

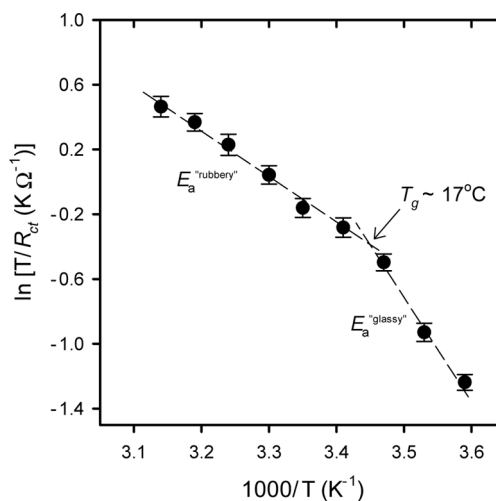


Figure 4. Arrhenius-type plot showing the dependence of $\ln(T/R_{ct})$ on the inverse temperature (T^{-1}). At $T = T_g$, there is a marked difference in the slope of the correlation line, indicative of a higher activation energy, E_a .

$1000/T$. As already shown for this kind of experiment, T/R_{ct} is proportional to the reaction rate constant k (see Supporting Information and references therein). From this figure, it is evident that the electron transfer requires different activation energies whether the process occurs below or above T_g . Activation energy values calculated from the experimental data are 53.3 and 26.6 kJ/mol for temperature domains below and above T_g , respectively.^{26,27} These results indicate that the activation energy for the electron transfer taking place within the brush in the “glassy” state is twice the activation energy in the “rubbery” state.

This quantitative comparison of activation energies further confirms the critical role of the thermally activated macromolecular organization and the mobility of the grafted polymer chains in defining the electron transfer characteristics of a chemically modified electrode.²⁸ It is a well-known fact that T_g has a significant impact on the diffusion of molecular species through the macromolecular matrix.²⁹ In most cases involving ionic transport through polymeric materials, increasing temperature above T_g is reflected as a sudden increase in diffusion coefficient values.³⁰ This feature is commonly ascribed to changes in segmental mobility and the formation of free volume between polymer chains that greatly facilitate the diffusion of small molecules through the “rubbery” film. From the EIS data, we were able to estimate the diffusion coefficients of $\text{Fe}(\text{CN})_6^{4-/3-}$ (see Supporting Information for details) at different temperatures, and the resulting values are consistent with prior reports.³¹ As seen in Figure 5, there is a significant jump in D upon increasing temperature above T_g . Diffusion of

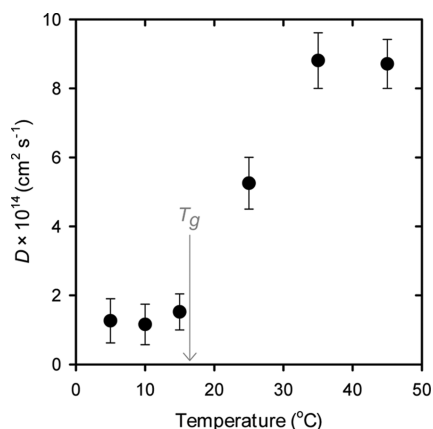


Figure 5. Representation of the diffusion coefficient (D) of the redox probe as a function of temperature. For the sake of clarity, the glass transition temperature ($T_g \sim 17$ °C) is indicated by a gray arrow.

the redox probe is approximately nine times faster above T_g . If we consider that many applications of polymer brushes demand new strategies to manipulate and/or activate transport and permeability of small molecules passing through these films, the manipulation of D using T_g as a thermal trigger can be an interesting practical step to achieve such a goal.

In conclusion, we showed for the first time the capabilities of Faradaic impedance spectroscopy as a tool to estimate the glass transition temperature of ultrathin polymer brushes at solid–liquid interfaces.³² This is a fundamental parameter in thin films that accounts for the presence of thermally induced structural transitions. To measure the glass transition temperature, the charge transfer resistance was measured as a function of temperature, and the temperature corresponding to the near discontinuous change in R_{ct} was identified as T_g . Further results from the modeling of the impedance response as a function of temperature enabled the estimation of the diffusion coefficient of the redox probes close to the thermal transition temperature. Impedance measurements corroborated the typical scenario in which diffusion coefficients sharply increase at temperatures higher than T_g . From the functional viewpoint, our results gain particular relevance not only because this is the first estimation of T_g in polyelectrolyte brushes at solid–liquid interfaces but also because we demonstrate that this transition occurs close to room temperature.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(26) It is worth mentioning that polyelectrolyte brushes are in collapsed conformation at all experimental temperatures due to the high concentration of perchlorate ions (0.1 M NaClO₄). Thus, it is very unlikely that a decrease in temperature might lead to a further collapse of the structure within our experimental temperature domain. In situ ellipsometric measurements corroborated that the brush thickness remained independent of the electrolyte temperature within the working temperature range. Further details can be found in: (a) Farhan, T.; et al. *Soft Matter* **2005**, *1*, 66–68. (b) Azzaroni, O. *Macromolecules* **2005**, *38*, 10192–10199. (c) Rodríguez-Presa, M. J.; et al. *Anal. Chem.* **2009**, *81*, 7936–7943. (d) Ramos, J. J. I. *Assembly and Physico-Chemical Characterization of Supramolecular Polyelectrolyte Nanostructures*, PhD Thesis, Doctor Europeus, San Sebastián, Spain, 2011.

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