

## Rheology of dopamine containing polymers

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### ABSTRACT

This short paper gives an overview of the rheological properties that were observed for random-copolymers of n-isopropylacrylamide and dopamine methacrylate in different media reacting to different cations and under different pH. In general, the behaviour is solution like at low pH (<7), while at pH above 7.5 a supramolecular gel is found.

### INTRODUCTION

While the rheology of different polymer solutions has been the subject of rheological research, studies focussing on the rheological behaviour of associative polymers have been scarce until the last years. The behaviour of associative groups with easily tuneable associativity has focused on several types of groups, among which dopamine groups are very versatile in terms of bonding strength and pH-tuneable behaviour. The rheology of polymers containing these groups has only been studied in the last years.

Two different systems were studied in general. The groups of Waite and of Messersmith characterized polyethylene oxide chains (usually of star-like

topography) with telechelic dopamine groups.<sup>1-6</sup> Our group used random copolymers of n-isopropylacrylamide (NIPAM) and dopamine methacrylate (DMA), which, in addition to the pH- and ion-sensitivity stemming from the dopamine functionality, also features a distinct temperature sensitivity in aqueous environment due to the thermoresponsiveness of NIPAM.<sup>7-11</sup>

Dopamine groups are the most common type of catechol, featuring a benzene ring with two hydroxyl-groups, which at sufficiently high pH – ca. pH 7.5 becomes protonated and, therefore, active in accepting sufficiently small cations. It is well known that Fe<sup>3+</sup>-ions complex strongly with catechol groups, as this is the main bonding mechanism of certain types of mussels (*Mytilus* species) on rocks,<sup>12</sup> hence, the term “mussel-inspired” polymers for dopamine-group containing polymers.

However, it should also be mentioned that the Achilles heel of dopamine is its sensitivity to oxidation – termed *catechol tanning*,<sup>13</sup> limiting its use in applications, where the acid-induced detachment of dopamine-cation bonds is essential for a long time.<sup>8</sup>

In this short article, we will mostly focus on the question of rheological properties of p(NIPAM-co-DMA) random copolymers with a DMA-content of 5 mol%, which we abbreviate as NIDO5%.

## EXPERIMENTAL

NIDO5% was radically polymerized from commercially available NIPAM (98% Aldrich) and self-synthesized dopamine methacrylate. Nuclear magnetic resonance found a DMA-content of 4.9 mol%. The molar mass  $M_n$  was found to be 2800 g/mol by osmometry and the polydispersity index was found to be 2.1 by GPC. Full experimental details of synthesis of DMA and NIDO5% as well as of the analytical characterization are given elsewhere.<sup>8</sup>

Gels were prepared by making a solution of NIDO5% at a concentration of 10 or 20 wt.% in water, dimethylformamide (DMF) or Dimethylsulfoxide. Subsequently, the desired multivalent cations were added as their chloride solutions (in case of aqueous solutions).

### Rheology

The rheological characterization was performed on a Malvern Kinexus Pro stress controlled rheometer using 20 mm parallel or 20 mm/2° cone-plate geometry. The temperature was controlled by a Peltier heating system in the lower plate. The solvent of the systems was contained in the geometry by establishing a solvent saturated atmosphere using a solvent trap with liquid seal.

The use of parallel plate geometry proved necessary for some of the samples, namely  $Fe^{3+}$  containing gels, as it was not possible to compress the gel into shape with a cone and plate geometry. The minute gap between the truncated cone tip and the lower plate exerted such a strong normal force that the gel phase separated and, consequently, a

small white disk of NIDO5% was found below the tip surrounded by a NIDO5%-depleted polymer solution. This, of course, has to be avoided and, hence, especially the harder gels had to be inserted into the rheometer with great care and by avoiding a significant compressive force during closing the gap.

Several different test setups were used for the characterization, but for this article we restrict ourselves to frequency sweeps and strain sweeps as well as time sweeps after the strain sweep to test the self-healing behaviour of the gels. All experiments were performed at 10 or 15°C in order to exclude any effect of the lower critical solution temperature (LCST) due to the NIPAM, which for NIDO5% at pH=9 with  $B^{3+}$ -ions is found to be at around 29°C, i.e. slightly lower than for pure PNIPAM (32.9°C<sup>14, 15</sup>) due to the increased hydrophobicity of NIDO5% due to the catechols.

## RESULTS AND DISCUSSION

Fig. 1 shows strain sweeps performed for gels supramolecularly crosslinked with trivalent cations. It is obvious that the different ions lead to very different moduli. For all measurements, the ion loading is 1/3 eq., which means that one positive “charge” is available for each catechol group. While  $Cr^{3+}$  leads to  $G'(\gamma_0$  in lve range) around 120 Pa,  $B^{3+}$  shows ca. 1200 Pa. However,  $Fe^{3+}$  and  $Al^{3+}$  show  $G'(\gamma_0)$  around 4500 Pa with  $Al^{3+}$  being slightly higher than  $Fe^{3+}$ . Two different kinds of strain sweeps are observed:  $B^{3+}$  and  $Fe^{3+}$  exhibit a peak in  $G''(\gamma_0 \approx ca. 100\%)$  but no peak for  $G'(\gamma_0)$ , while  $Cr^{3+}$  and  $Al^{3+}$  exhibit a clear peak in  $G'(\gamma_0)$ . In general, this kind of behaviour is found mostly for systems, which can be stretched to some degree, as pointed out in the seminal work of Sim et al..<sup>16</sup>

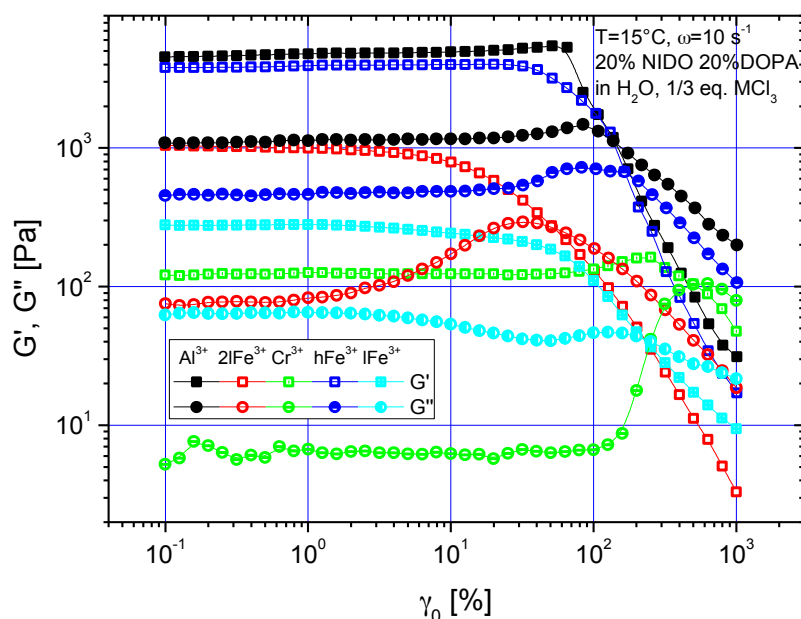


Figure 1. Strain sweeps of aqueous solutions of NIDO5% with trivalent ions,  $c=20$  wt% in  $\text{H}_2\text{O}$ ,  $\text{pH}=3$  (low pH) or  $\text{pH}=8$  (high pH)

Among all the cations tested, only  $\text{Fe}^{3+}$  is able to form a rather weak gel, while all other ions lead to a small change in Newtonian viscosity of such polymer solutions, but have no rheological effect otherwise. When comparing the  $\text{Fe}^{3+}$ -gels at low and high pH, it is obvious that the general features are the same, although the modulus is significantly lower for the low pH-gel. When looking more closely, however, it appears that 2 curvatures are found for the low pH gel (at  $\gamma_0 \approx 3\%$  and  $\gamma_0 \approx 70\%$ ), while only one is found for the high pH-gel.

The lack of interaction between ions and dopamine groups at low pH can also be observed from the fact that mixing the ions with the polymer solution results in no significant effect on the solution colour (in case of ions having a colour in aqueous solution, while the addition at high pH leads to a clear colour change along with the gelation. For example, the greenish  $\text{Fe}^{3+}$  (no polymer) changes to a rather strong olive green (gel, high pH – the gel at low pH is more greenish) or  $\text{Ni}^{2+}$  changes from slightly yellow to dark brown.

The supramolecular character of the gels can be easily assessed from the fact that a deformation  $\gamma_0^{\text{max}}=1000\%$  leads to complete self-healing as shown in Fig. 2a on the example of gels produce with  $\text{Fe}^{3+}$  ions at  $\text{pH}=3$  and  $\text{Cr}^{3+}$  at  $\text{pH}=8$ . In both cases, the initial moduli are rapidly recovered within ca. 30 s. However, it is remarkable to see that the two gels have one clear difference in their behaviour. The gel made with  $\text{Fe}^{3+}$  ions at  $\text{pH}=3$  increases (rather quickly) to reach the values of  $G'$  and  $G''$  before the strain sweep. The same dynamics are also found for  $\text{Fe}^{3+}$  ions and  $\text{Al}^{3+}$  at  $\text{pH}=8$  (Fig. 2b), but significantly slower, which can be easily understood from the higher moduli, which lead to lower chain mobility, as the fraction of unbonded chains must be the higher the modulus.

For the  $\text{Cr}^{3+}$  ions containing gel, however, we find the counterintuitive result that the modulus is higher in the beginning but then decreases subsequently to reach the original value after some time (ca. 250 s in this case).

In all cases, the phase angle  $\delta$  decreases with increasing time.

While it is clear that there must be some reason behind these different behaviours it is rather difficult to draw conclusions, as the whole matter is still far from understood.

The previously published results on NIDO5% based gels showed that the strain sweeps do not show a maximum in  $G'(\gamma_0)$ , while unpublished data for  $B^{3+}$ -NIDO5% gel at 10 wt.% concentration shows a weak peak around  $\gamma_0 \approx 300\%$ , just like the  $Cr^{3+}$ -NIDO5% gel, which also have roughly the same modulus. Furthermore, this sample also shows a weakly decreasing  $G'$  and  $G''$  in the time sweep following the strain sweep.

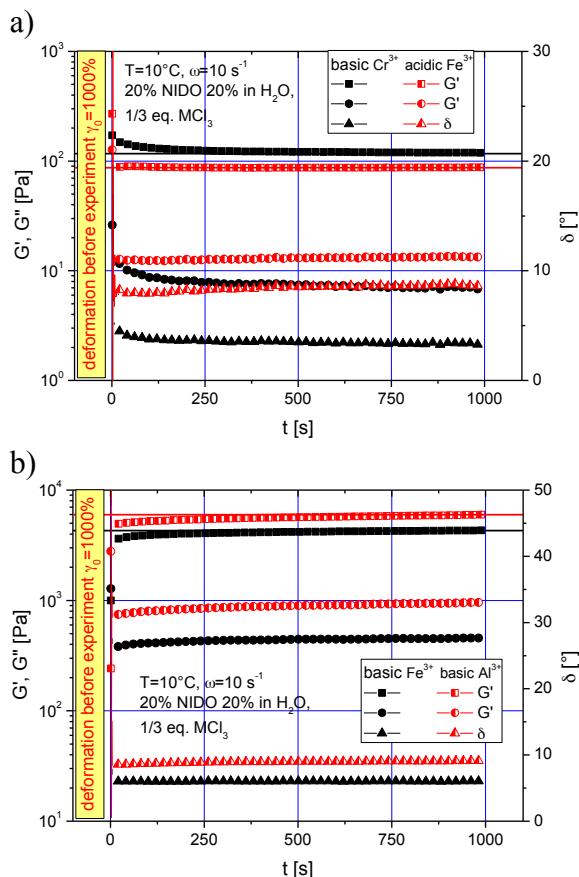


Figure 2. time sweeps following strain sweeps with  $\gamma_0^{\max}=1000\%$  of aqueous solutions of NIDO5% a) with  $Fe^{3+}$  ions at pH=3 and  $Cr^{3+}$  at pH=8, b) with  $Fe^{3+}$  ions and  $Al^{3+}$  at pH=8, c=20 wt% in  $H_2O$

Hence, the preliminary is drawn that the high shear leads to a metastable structure, which is stiffer than the normal network structure. This structure, however, returns back to equilibrium structure within minutes.

Gels with a higher modulus do not show this metastable structure, as can be seen from the fact that the sample recovery from  $\gamma_0^{\max}=1000\%$  is an increasing one for  $G'$  and  $G''$ , while  $\delta$  decreases as recovery time proceeds. The decrease in phase angle can be explained by the structural perfecting, which slowly reduces the number of dangling segments and, thus, decreases the number of possible energy dissipation modes.<sup>17</sup>

The strain sweeps in general show that the nonlinearity onset is in the typical range for polymer solutions, melts, and also gels (lve limit around 50%). In general, a lower modulus means that the nonlinearity limit is shifted to higher  $\gamma_0$ . This was also observed for other solutions produced with the same NIDO5% polymers under completely different solution conditions, suggesting some universal scalability, which needs further exploration.

However, the question as to why  $B^{3+}$  and  $Fe^{3+}$  (high and low pH) do not exhibit a peak in  $G'(\gamma_0)$ , while  $Cr^{3+}$  and  $Al^{3+}$  with comparable moduli do exhibit such a maximum.

In general, it is established that the  $G'$ -maximum in strain sweeps is related to network chain stretchability, but it is completely unclear what the difference in gel structure between e.g.  $Fe^{3+}$  and  $Al^{3+}$ -gels is to lead to such obvious differences. It should be mentioned that the shown experiments only represent a fraction of the experiments done for these systems. In case of these 2 gels, the same experiments were performed at many other temperatures and for all temperatures below the LCST, the qualitative finding that  $Al^{3+}$ -gels have a  $G'$ -maximum in strain sweeps persists, while their  $Fe^{3+}$ -counterparts do not.

Although it is not satisfactory, we have to conclude with the statement that while some of the differences can be explained based on previous experience with associative polymers, several of the effects cannot be satisfactorily explained with the currently established knowledge and requires deeper investigations in the future.

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