



# Competition and Cooperation of Electrostatic Repulsion and Hydrophobic Aggregation:

## The Structural Evolution of Thermal-responsive Weakly Charged Polyelectrolytes

Author: NO.11029018 Yilan Ye Supervisor: Prof. Qiang Zheng

### Introduction

Electrostatic repulsion and hydrophobic aggregation are two fundamental interactions in both biologic and synthetic systems. In most cases, these two interactions coexist while playing different roles, endowing the system with diverse properties and functions.

Starting with the simplest situation, researchers investigate a single chain with ionic groups and hydrophobic groups randomly distributed. This type of polymer is termed as hydrophobically modified polyelectrolyte (HMP). Rubinstein assumes that to balance the electrostatic repulsion and surface tension due to hydrophobicity, HMP would adopt *necklace* conformation to make its free energy lowest.

However, when HMP concentration increases, single chains would overlap and interact with each other, leading to more complex situations and many questions require exploration.

Among most of the research on this issue, HMP were synthesized through copolymerization of a series of ionic monomers and alkylated monomers. Yet the limitation of this method is difficulty in tuning the degree of hydrophobicity. In the present work, the authors take the advantage of N-isopropylacrylamide (NIPAM), whose homopolymer has LCST=32 °C. The copolymer of NIPAM and a few amount of ionic monomers would experience continuous change in hydrophobicity from good solvent to poor solvent upon heating, and more details about the interplay of electrostatic repulsion and hydrophobic aggregation would be found.

### Materials and Method

The samples were synthesized by copolymerization of NIPAM and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) at 10 °C. Based on the percentage of NIPAM, samples are named as N99, N97, N95 and N90. Since the contents of AMPS are below 10%, the copolymer is also a kind of weakly charged polyelectrolyte without counterion condensation. The homopolymer of NIPAM is named as PNIPAM. The reactivity ratio tested at 30 °C of NIPAM and AMPS is  $r_{NIPAM}=1.00$  and  $r_{AMPS}=0.11$ . Calculation of average sequence length of NIPAM and AMPS shows that AMPS exists individually among blocks of NIPAM.

Table 1 Sample information

Sample	NIPAM %	$M_n$ / kDa	$M_w$ / kDa	$M_w/M_n$
PNIPAM	100	43	101	2.36
N99	98.6	46	107	2.31
N97	97.3	70	144	2.07
N95	94.4	81	152	1.87
N90	91.0	43	122	2.11



### Results and Discussion

#### 1. Solution in good solvent

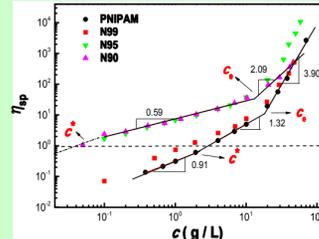


Fig. 1 Concentration dependence of Specific Viscosity  $\eta_{sp}$  of sample PNIPAM, N99, N95 and N90 at 20 °C.

Based on the Scaling theory, solution properties of neutral polymer and polyelectrolyte are significantly different. In Fig. 1, N99 exhibits the same scaling exponent as neutral polymer PNIPAM, while N95 and N90 obey the typical rule of polyelectrolyte. It shows that only 5% of ions are enough to dominate the static and dynamic property of the polymer chain. Moreover, concentration regions of solution could be divided by recognizing critical concentration  $c^*$  and  $c_c$ .

#### 2. Solution of "necklace"

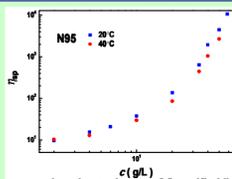


Fig. 2 Concentration dependence of Specific Viscosity  $\eta_{sp}$  of sample N95 at 20 °C and 40 °C.

For N95 at 40 °C, on one hand segments of PNIPAM tend to collapse into globule due to hydrophobicity, on the other hand electrostatic repulsion from anionic monomers AMPS is so dominant that they keep the polymer chain stretched. This could be seen in Fig. 2 where  $\eta_{sp}$  changes slightly from 20 °C to 40 °C. In balance, polymer may turn out to be *necklace* like.

#### 3. Thermal-responsibility of entangled solution

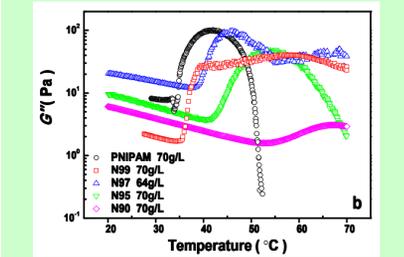
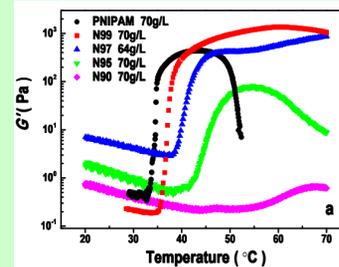


Fig. 3 Temperature dependence of (a) Storage Modulus  $G'$  and (b) Loss Modulus  $G''$  of sample PNIPAM, N99, N97, N95 and N90 at heating rate of 0.5 °C/min.

Entangled solution has complex structural evolution upon heating. For PNIPAM shown in Fig. 3, below 32 °C modulus decrease due to decrease of solution viscosity; above 32 °C, abrupt increase of modulus indicates that hydrophobic aggregation leads to intermolecular structures; upon 45 °C, a second transition appears and modulus goes down steeply as the result of macroscopic phase separation. As ion contents increase from PNIPAM to N90, transition temperature increases and the trend of transition becomes much milder. Moreover, upon heating N95 and N90 also present a second transition trend, while it is totally different from that of PNIPAM.

Fig. 4 presents specific status of each sample at certain temperature. Below transition temperature, N99, N97 and N95

#### 4. Structural evolution of entangled solution

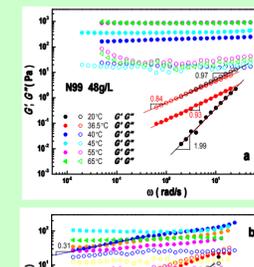
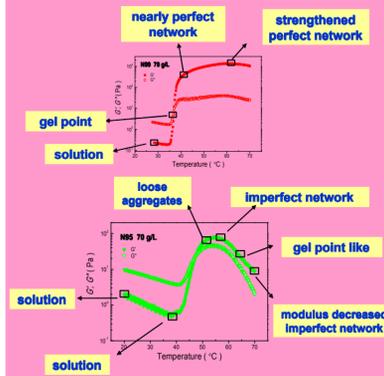


Fig. 4 Frequency dependence of Storage Modulus  $G'$  and Loss Modulus  $G''$  of sample (a) N99, (b) N97 and (c) N95 after heating at the rate of 0.5 °C/min from 20 °C to specific temperature

all exhibit classic solution dynamics. Above it, N99 becomes gel of nearly perfect network in quick time; N97 gradually change from gel of imperfect network to nearly perfect network; For N95, gel with imperfect network is formed at above 56 °C and modulus of the gel decrease upon further heating, which may be related to condensation of counterions.

#### 4. Illustration of structural evolution of entangled solution



#### 5. Dual thermal-responsibility and structural evolution of solution mixture in heating and cooling procedure

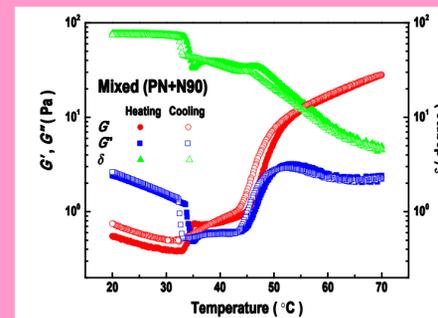


Fig. 5 Temperature dependence of Storage Modulus  $G'$  and Loss Modulus  $G''$  of mixture of PNIPAM and N90, Mixed (PN+N90), containing PNIPAM 15g/L and N90 22g/L at the heating rate of 1 °C/min.

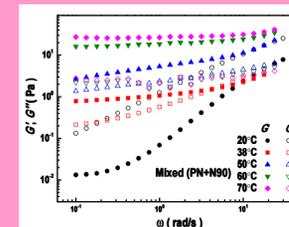


Fig. 6 Frequency dependence of Storage Modulus  $G'$ , Loss Modulus  $G''$  and Loss Angle  $\delta$  of mixture of PNIPAM and N90, Mixed (PN+N90), containing PNIPAM 15g/L and N90 22g/L, after heating to specific temperature at the rate of 1 °C/min.

Temperature dependence of the mixed sample, Mixed (PN+N90), in Fig. 5 is very interesting. Unlike a simple superposition of the trend of PNIPAM and N90, their mixture shows that the two polymer interact greatly upon heating. At 32-45 °C, PNIPAM undergoes phase transition yet hydrophobic aggregation is carefully suppressed by N90, whose ionic groups would possibly surround PNIPAM to protect it from water. Above 45 °C, hydrophobicity develops further and N90 fails to offer more protective ions. As a result, hydrophobic aggregation from both PNIPAM and N90 dominate the structural evolution afterwards. Fig. 6 shows that at 38 °C, the mixture solution deviates from classic solution dynamics and some intermolecular structure is formed; at 50 °C gel of imperfect network is formed; from 60-70 °C the network becomes nearly perfect, while its modulus is much lower than that formed by PNIPAM, N99 and N97.

#### 6. Influence of heating rate

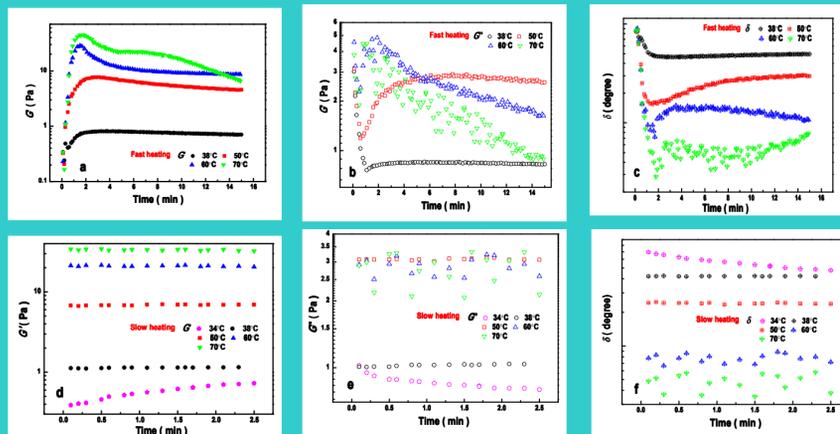


Fig. 8 Time dependence of Storage Modulus  $G'$ , Loss Modulus  $G''$  and Loss Angle  $\delta$  of Mixed (PN+N90) through (a-c) fast heating, Jumping from 20 °C to specific temperature and (d-f) slow heating at the rate of 1 °C/min from 20 °C to specific temperature.

In Fig. 8, through slow heating, almost equilibrium structure could be obtained when temperature is above the transitional region (32-35 °C). On the contrary, fast heating would lead to different situation, especially when temperature is above 60 °C. The peak of Storage Modulus  $G'$  at 60 and 70 °C indicates that high temperature propels hydrophobic aggregation rather than electrostatic repulsion. When network is formed in a sudden and phase separation is about to happen, electrostatic repulsion begins to function to stop macroscopic phase separation and to suppress the breakdown of network structure.

### Conclusion

Electrostatic repulsion and hydrophobic aggregation has competitive balance for hydrophobically modified polyelectrolytes. Above the LCST of NIPAM, these two types of interaction would be dominated in different temperature region and solution structure keeps evolution to establish new balance. Different ion contents lead to distinctive thermal behavior varying from PNIPAM to N90.

On the other hand, when PNIPAM was mixed with ionic copolymer N90, the interaction of electrostatic repulsion and hydrophobic aggregation is more cooperative rather than competitive. In this case, in order to lower the free energy of the mixture, N90 would try its best to protect PNIPAM from macroscopic phase separation. In the end, the system exhibits dual thermal-responsibility, which is completely different from a simple superposition of the trend of PNIPAM and N90.