



Shear-induced self-thickening of chitosan-graft-polyacrylamide aqueous solution

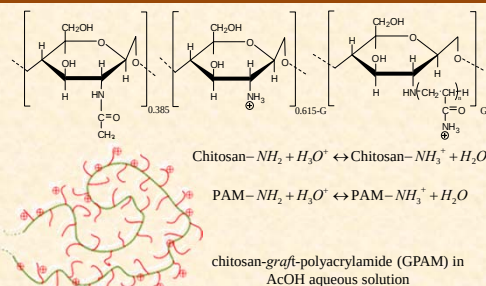
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Introduction

A remarkable shear induced self-thickening (SIT) of chitosan-graft-polyacrylamide (GPAM) aqueous solution was observed. After GPAM solution was subjected to a high-rate shear for several minutes, their viscosities recovered once removing shear and then a much higher zero shear viscosity (η_0) than the original one appeared. In fact, the self-thickening differs from conventional shear thickening or viscous recovery as reported previously. The thickening was proved to be the results of enhanced scale of GPAM aggregations in aqueous solution, and the mechanism of aggregations was proved to be intermolecular hydrogen bonding effects. Besides, the shear-induced self-thickening seems to be facile, maintainable and easily controllable by changing shear conditions.^{1,2}

Materials



Sample	GPAM1	GPAM2	GPAM3
Grafting Ratio (%)	70.8	324	481
PDI	2.31	1.62	1.60

Graft polymerization of PAM onto CS was carried out using Ceric ammo-nium nitrate (CAN) as the initiator under nitrogen (N_2) atmosphere at 45 °C for 4 h. In all rheological tests, original samples were dissolved by 0.2% (v/v) AcOH solution.

Rheological behaviors

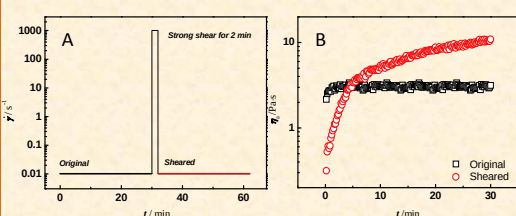


Figure 1. (A) Design of the shear rate in SIT test; (B) SIT of 1 wt% GPAM1 solution monitored at 0.01 s^{-1} after being sheared at 1000 s^{-1} for 2 min.

Figure 1 presents the summary of reported SIT phenomenon of GPAM solution. Figure 1A gives the variations of shear rate with time during the shear treatment process. Once ceasing strong shear, apparent viscosity (η_a) of GPAM would recover soon, then increase sequentially and the final η_a after shear treatment are much higher than the original ones, as shown in Figure 1B.

Figure 2A gives the comparison of viscosity evolutions for PAM, CS and GPAM in recovery step. Here, the dash lines represent the apparent viscosities of original samples and they were measured under steady shear at the same shear rate as recovery step. As expected, the shear thinning of PAM (flexible chains) did not recover in 30 min while CS (semiflexible chains) recovered immediately. Differing from them, all GPAM samples presented an obvious thickening phenomenon and the final η_a became much higher than original ones.

Figure 2B displays the steady flow curves of the original and thickened samples undergoing above experimental processes. Undergoing this treatment, η_a of GPAMs at low shear rate increase obviously to varying degrees while it is not shown for CS, PAM, and many other polyelectrolytes. However, at high shear, η_a of thickened samples are the same as the original ones, indicating that the structural changes of GPAM after thickening could be completely damaged by strong shear.

Acknowledgements

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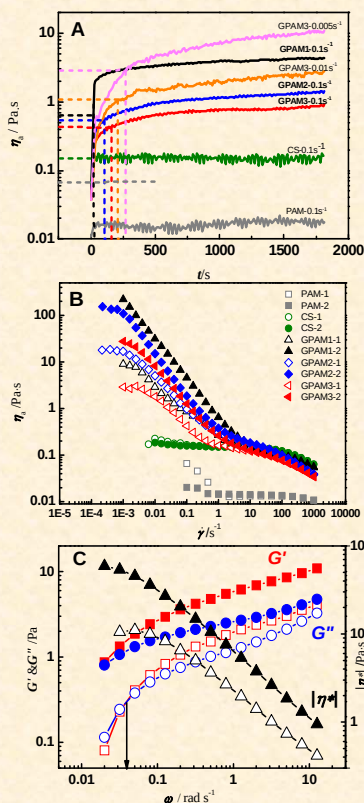


Figure 2. (A) Thickening processes for 1 wt% GPAM solutions after being sheared at 1000 s^{-1} for 2 min (CS, 1 wt%; PAM, 1 wt%). (B) Steady flow curves of 1 wt% PAM, CS and GPAM1~3 solution before (open symbols, 1) and after (solid symbols, 2) shear-induced thickening for 30 min. (C) Frequency (ω) dependences of dynamic storage modulus (G' , square), dynamic loss modulus (G'' , circle), and complex viscosity ($|\eta^*|$, triangle) for 1 wt% GPAM3 solution before (open symbols) and after (solid symbols) thickening. Frequency sweeps were performed at 1% strain amplitude proven to be in linear viscoelastic region.

Figure 2C shows the oscillatory frequency sweep results of original and thickened GPAM solutions. Besides, increasing $|\eta^*|$ of the sheared sample is consistent with that of η_a in steady shear test. On the other hand, Maxwell model is not suitable for fitting the results, suggesting that there is no real homogeneous network in GPAM solution and the observed thickening effect may be attributed to other intermolecular structures, like aggregations.³

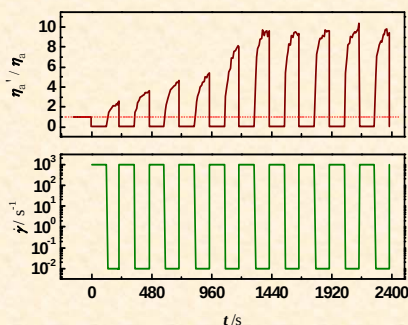


Figure 3. Controllable thickening for apparent viscosity at 0.01 s^{-1} with tuned shear rate for 1 wt% GPAM1. η_a/η_0 means the thickening ratio and $\eta_a/\eta_0 > 1$ is the sign that the observed viscosity surpasses the origin.

Interestingly, the increased viscosities of GPAM are controllable in following three cases. For the first case (case 1), as shown in Figure 2A, controlling the time of recovery can attain certain η_0 ranging from the origin to final equilibrium thickening viscosity. For case 2, multiple repeated shearing-recovery treatments can be adopted to improve the thickening after strong shear. As shown in Figure 3, η_a recovers immediately once removing high shear and it will completely recover in less than 10 s after several cycles. For case 3, after several repetitions the thickening amplitude seems to reach the saturation and then a good repeatability appears, showing a rapid switchable thickening.

Hydrogen bonding aggregations

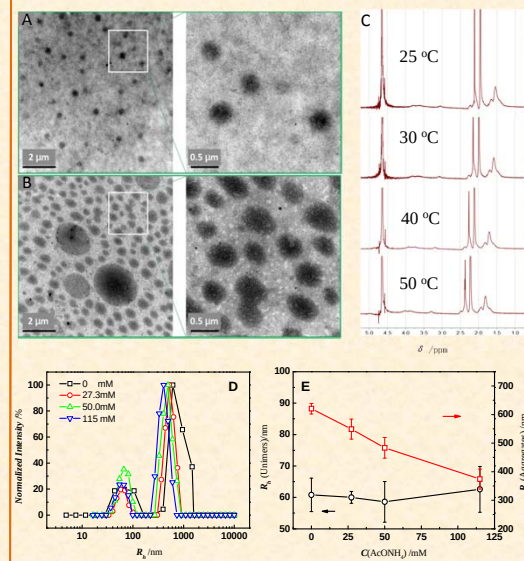
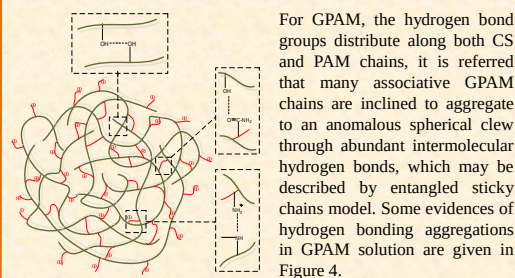
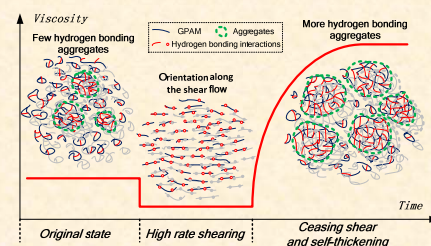


Figure 4. TEM observations of 0.4 wt% GPAM3 in 0.2 % (v/v) AcOH solution before (A) and after (B) SIT for 30 min; (C) ^1H -NMR results of GPAM solutions at different temperatures (25 °C, 30 °C, 40 °C, 50 °C). $C(\text{GPAM3})=0.3 \text{ wt\%}$, $C(\text{AcOH})=0.2 \text{ \% (v/v)}$; (D) Influences of hydrogen bond breaker, ammonium acetate (AcNH_4), on the GPAM aggregations in 0.005 wt% solution at 20 °C: a typical bimodal distribution of hydrodynamic radius (R_h); (E) Comparison of R_h for aggregates and unimers in the solutions with different AcNH_4 concentrations.



For GPAM, the hydrogen bond groups distribute along both CS and PAM chains, it is referred that many associative GPAM chains are inclined to aggregate to an anomalous spherical clow through abundant intermolecular hydrogen bonds, which may be described by entangled sticky chains model. Some evidences of hydrogen bonding aggregations in GPAM solution are given in Figure 4.

Conclusions



GPAM solutions present a special shear induced self-thickening behavior, which is different from traditional shear thickening and rapid recovery after shear thinning. The thickening amplitude would be remarkable if the GPAM samples with the appropriate grafting ratios are sheared at a high shear rate and thickening at static state for enough time. Moreover, repeated shear-recovery treatments enhance the recovery and thickening rate and there will be a rapid response thickening which could be controlled. The mechanism of this shear induced thickening is proved to be the formation of larger scale hydrogen bonding aggregations after strong shear.

References

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