

Note

EFFECT OF CRYOGENIC AND HEATING TREATMENT ON THE SOLUTION PROPERTIES OF NITROCELLULOSE*

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Abstract The effect of cryogenic and heating treatment on the solution properties of rigid polymer nitrocellulose (NC) in dilute tetrahydrofuran solution were studied with a sealed viscometer and a size exclusion chromatograph (SEC), respectively. The experimental results show that the relative viscosity of NC solution decreases after repeated freezing-thawing treatment. The decreased viscosity value of NC could not be restored but decreased further after the solution being re-heated. The experimental results of SEC are fully consistent with that of viscosity measurements. It is believed that the effect of two treatments on NC solution both causes the apparent hydrodynamic volume to decrease. But they are assumed to be ascribed to different mechanisms.

Keywords: Nitrocellulose; Freezing-thawing cyclic treatment; Heating treatment; Viscosity; Size exclusion chromatograph.

INTRODUCTION

It is an interesting research topic to study the solution properties of polymer after different thermal treatment. In 1960s, Berlin^[1] introduced freezing-thawing cyclic process to study the effect of cryogenic treatment on the dilute polymer solution. Later, some researchers^[2–9] have accepted the concept that long-chain macromolecules in solution undergo degradation after cryogenic treatment. This conclusion was reached from measured size exclusion chromatographic^[2–6], and viscometric^[7–9] data. The phenomena of decreasing solution viscosity and increasing retention volume of SEC were regarded as the result of degradation of the polymer chain. In 1990s, Cheng and Liu *et al.*^[10] studied the extremely dilute aqueous solution of polyvinyl alcohol (PVA) by the freezing-thawing cyclic treatment, and found that the decreased viscosity value of PVA would come back after the solution being re-heated. Then, Cheng and Wang *et al.*^[11, 12] further studied the α -polystyrene (aPS) toluene solution by LLS after the same treatment, and directly detected the molecular weight before and after cryogenic treatment, and found that the molecular weight of the polymer had never changed, but the constant of the specific refractive index increment had produced some difference. They concluded that the change of the polymer chain size by cryogenic treatment should be ascribed to its conformation change and not to cryogenic degradation. It is of great help to learn the behavior of polymer solution after cryogenic or other thermal treatment.

However, PVA and aPS are both flexible chain polymers, and how about the behavior of the rigid or semi-rigid polymer solution after being dealt with cryogenic treatment? Nitrocellulose^[13, 14], which is a well-known cellulose derivative, is also a rigid polymer. In this paper, the effect of cryogenic and heating treatment on the

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solution properties of NC in dilute solution has been studied with a sealed viscometer and SEC. The results of NC solution properties have been compared to that of flexible polymer systems, and the available change mechanisms of the conformation have been discussed respectively.

EXPERIMENTAL

Materials

The substitution degree of NC is about 2.40, and its apparent weight and number average molecular weight, based on standard samples of polystyrene, are 17.4×10^4 g/mol and 7.57×10^4 g/mol, respectively, the ratio of weight- to number-average molecular weight is about 2.30 as determined by SEC. Tetrahydrofuran (THF) is AR grade reagent, which was dried for 2 days and distilled before use.

Freezing-Thawing Cyclic Treatment

A known amount of NC was dissolved in THF to prepare a solution with a concentration of 1.00×10^{-3} g/mL in a sealed tube. The tube was immersed into liquid nitrogen for 3 min, then it was taken out and thawed at the room temperature. This process was called a freezing-thawing cycle, namely $N = 1$.

Heating Treatment

The solution was prepared by the same method as described before, then put into a water bath and kept the temperature at 100°C for 2 h.

Viscosity measurement

In this work, a sealed viscometer was designed and used especially for volatile solvent-based solutions. Figure 1 shows schematically the slightly modified viscometer, which is composed of an Ubbelohde viscometer, rubber tubings, a T-tube, three-way stop-cock and back pressure bulb. Before installing the modified viscometer, the Ubbelohde viscometer was thoroughly cleaned by repeatedly rinsing and soaking for 2 days with deionized water and finally drying at 110°C after every measurement. And the efflux time of pure THF in this viscometer is 111 s at 30°C .

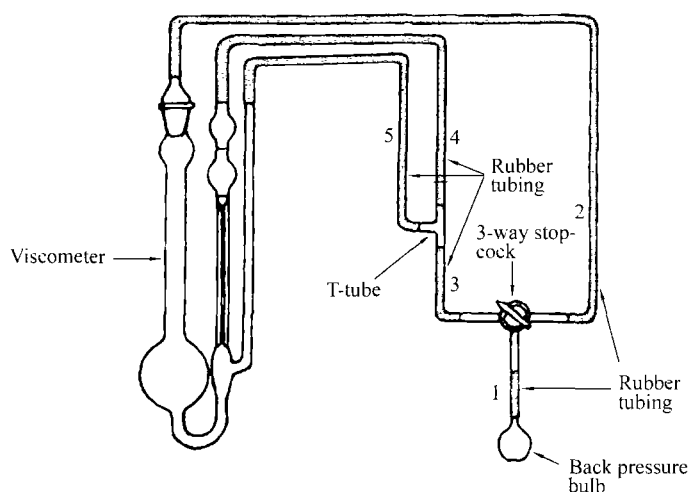


Fig. 1 The Schematic diagram of the sealed viscometer

Size-Exclusion Chromatography

All SEC analyses were conducted with a Waters Associates GPC Model210 equipped with RI R401 detector (THF as elution solvent), Model510 pump. Narrow distribution standard polystyrene samples at concentration of 10^{-4} g/g were used for calibration. The column used consisted of μ -StyragelTM 10, 50, 10^2 , 10^3 nm gels (Waters Assoc.). The flow rate was kept at 1.00 mL/min at room temperature. An internal small molar mass standard was added into the sample solutions which was injected into the SEC column for correction of the retention time.

RESULTS AND DISCUSSION

The viscosity properties of the frozen dilute solutions of NC/THF were measured at 30°C in a sealed viscometer. In Fig. 2, it was found that the relative viscosity of NC/THF solution decreases from 1.30 to 1.27 after being repeated freezing-thawing treatment for 200 times. Then the temperature of the frozen solution was raised to 100°C, and kept at this temperature for 2 h. It is interesting to note that the viscosity of the solution at this time couldn't be restored after heating treatment like PVA system^[10], on the contrary, it decreases further. However, at the dilute concentration region, cryogenic treatment would make the polymer chains contract, and thus increase the available opportunity to form more intra-chain entanglement crosslinks, which will decrease the apparent hydrodynamic volume of the polymer chains, whereas heating treatment would be helpful to untie the formed intra-chain entanglement crosslinks and to restore to their original conformation, so it seems impossible to make the apparent hydrodynamic volume decrease further.

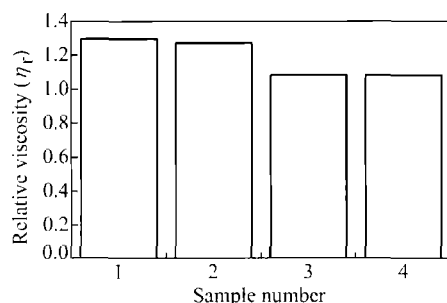


Fig. 2 The value of the relative viscosity of NC/THF solution after different treatments

- 1) Original solution; 2) Freezing-thawing cyclic treatment for 200 times to solution 1;
- 3) Reheating solution 2 at 100°C; 4) Heating treatment of solution 1

In order to compare the effect of two different treatments on the NC solution, the original NC solution was heat treated by two modes independently. In Fig. 2, it could be seen that the relative viscosity of the directly heat-treated solution decreased from 1.30 to 1.08, and the degree of this decrease is much higher than that by cryogenic treatment. In addition, if such a cryogenic treated NC solution was re-heated to 100°C for 2 h, the relative viscosity decreased further, and the viscosity value is very close to that of directly heat-treated solution.

The NC/THF solutions, which have experienced the same treatments as mentioned above in viscosity experiment, were also measured by SEC. The result is showed in Fig. 3. It can be seen that the retention volume of the heated solution increases evidently, whose value increases from 23.5 mL to 25.2 mL comparing to the original solution. But the change of the retention volume of the frozen NC/THF solution is very small, which are fully coincident with that from the viscosity experiment. It can be concluded that cryogenic and heating treatment both can decrease the apparent hydrodynamic volume of NC, and heating treatment is more effective than cryogenic treatment.

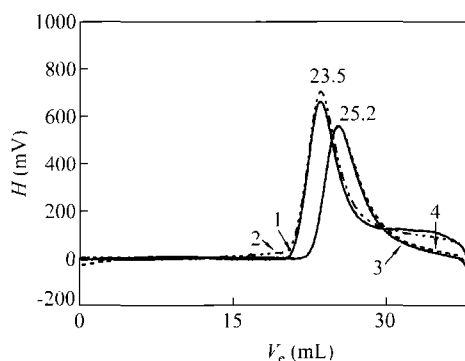


Fig. 3 SEC curves of different treatment NC/THF solution to the elution volume. The 1, 2, 3, and 4 are the same as in Fig. 2.

It is believed that the change of the solution properties after the two treatments are resulted from the transition of the polymer conformation in solution. Cryogenic treatment could make the NC chain contract, and decrease its apparent hydrodynamic volume, but NC chain is rather rigid and very difficult to contract too much, so the solution properties of the cryogenic treated solution change not so obvious. As for the heating treatment, it could not give a distinct mechanism yet. It is assumed that NC in solution tends to self-assemble, and form a multi-chain super-molecular structure by intermolecular hydrogen bonds. This structure is stable enough at room temperature, but it could be destroyed at higher temperature. So the hydrodynamic volume decreases remarkably comparing to cryogenic treated solution.

CONCLUSION

The freezing-thawing cyclic and heating treatments have been used to study the solution properties of rigid polymer NC solution respectively. The two treatments can both decrease the apparent hydrodynamic volume according to the experimental results, but there exist different mechanisms in the two treatments to affect the conformation of the chain. Cryogenic treatment would make the NC chain shrink, because of the rigidity of NC, the effect of the cryogenic treatment is not very notable, whereas the heating treatment is assumed to destroy the original multi-chain super-molecular structures of NC in solution to make the apparent hydrodynamic volume decrease. However, further experimental evidences are needed.

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