

The Properties of Poly(amide acid) Ammonium Salts in Water and Films Formation

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Abstract

Poly(amide acid) ammonium salt were prepared in a mixture of tetrahydrofuran and methanol. The properties of their water solutions were studied. We found that the temperature and concentration dependence of the viscosity follow the Arrhenius equations. The structures of these salts were characterized by $^1\text{H-NMR}$. The thermal imidization was studied by IR, DSC and TGA.

Key words: Poly(amide acid), Polyimide, Ammonium salt, Viscosity, Imidization.

Introduction

Polyimides have been known as advanced materials for various applications in high-tech fields, because of their high thermal stability, good mechanical and electrical properties etc^[1]. However, their processability is poor. Poly(amide acid) (PAA) precursor solutions are usually used as intermediates for process and film formation. But PAA's shelf life is short and sensitive to water and temperature. In order to improve the storage stability, several methods were applied, such as by using poly(amide ester)^[2-6], poly(amide acid) ammonium salt (PAAAS) etc. The researchers have been interested in PAAAS because it can be dissolved in water^[7-10]. The preparation of poly(bis(trialkylammonium) 4,4'-oxydiphenylenepyromellitamate) in the mixed solvent of tetrahydrofuran (THF) and methanol (MeOH) was reported and its structure was characterized with NMR by Y. Echigo et^[11]. The polyimide film obtained with this method exhibits low coefficient of thermal expansion (CTE). K. Horie et^[12] studied charge transfer complex in poly(amide acid) ammonium salt by UV absorption. We are also interested in the water-soluble precursor of polyimides for the application of coating. We tried to study on the properties of poly(amide acid) ammonium salts in water solution, where the relations of viscosity-concentration and viscosity-temperature are interesting. They are important for coating applications. There is no report on the above relations. We also used the mixture of THF and MeOH as the solvent. The PAA film can be obtained by casting on glass plate then being dried at room temperature. There was no imidization structure in PAA film and the film is different from that obtained from DMAc solution.

Experimental

Materials:

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) (polymerization grade) were purchased from industrial sources and were used as received. BTDA was used after recrystallization with acetic anhydride. Triethylamine (TEA), dimethylethanolamine (DMEA), THF, MeOH and other agents are analytical agent grade and were used as received.

Preparation of poly(amide acid)

20.02g (0.100 mol.) of ODA, 165.5g of THF and 41.2g of MeOH (THF/MeOH=8/2, by weight) were

added into a three-necked flask fitted with a mechanical stirrer and a thermometer. After ODA was dissolved, 21.8g (0.100 mol.) of PMDA powder was added into the above solution. The reaction temperature was controlled at room temperature by sufficient cooling. The solution was stirred at room temperature for several hours until a viscous homogeneous yellow PAA solution was obtained.

Preparation of PAA ammonium salts and their solutions

The above PAA solution was diluted with the same mixture of THF and MeOH to about 5 wt.% of concentration. Then an amine solution of THF and MeOH was added into the above diluted PAA solution slowly under stirring. PAA ammonium salt was precipitated and then the yellow solid salt was obtained by filtration, washing with THF/MeOH, drying under vacuum. The solid salts is soluble in water or MeOH, we can obtain water or MeOH solution of PAA salts. Their concentration is at about 10 wt%.

In additional, above PAA solutions were casted onto glass plates, then dried at room temperature for several hours. After PAA films were removed from glass plates, then continued to dry under vacuum. The dried PAA films were introduced into a water solution containing trialkyl amines and kept at room temperature for several days until they became homogeneous solutions. In that way, we can obtain a viscous water solution of PAA salt.

Preparation of polyimide films

PAA salts solutions were casted onto glass plates then heated at 80°C for 4hours, 120°C for 1hour, 160°C for 1hour, 200°C for 1hour, 250°C for 1hour consequently. The polyimide films were obtained by removing the films from glass plates.

Measurements

Infrared spectra (IR) were measured on films used an FTIR system of Nicolet 460. DSC and TGA were performed with a PE-7 instrument at a rate of 10°C/min in air atmosphere. ^1H -NMR was measured by JEOL FX90Q. Viscosity was measured with CS501-SP viscometer made by Chongqing Sida Instrument Factory.

Results and Discussion

Polyimide films and coatings have been applied in high technical fields. In order to avoid removing the organic agent e.g. DMAc, the water soluble polyimide precursor has been studied. The preparation and characteristics of poly(amide acid) ammonium salt precursors were reported. But their properties in water solutions has not been reported. They are important in the process of film casting and coating. We tried to study the properties of PAA salt in water solution by measuring their viscosity under various temperatures and concentrations. We found that the relations of viscosity-temperature and viscosity-concentration followed the Arrhenius equation, namely graphs of viscosity against logarithm-1/T and viscosity against logarithm-concentration logarithm were all linear in Fig. 1 and Fig.2. This group of straight lines are parallel lines for various components of BTDA-ODA copolymers (Fig.1). We can calculate the activation energy (ΔE) from Fig.1. But we found the water solutions became gels at 10wt.% at a temperature lower than 10°C, when the inherent viscosity of PAA was higher than 0.7dl/g. There exists a strong intermolecular Coulomb force in PAA salt because it is an ionic polymer. ΔE is the minimal energy required to overcome the Coulomb force.

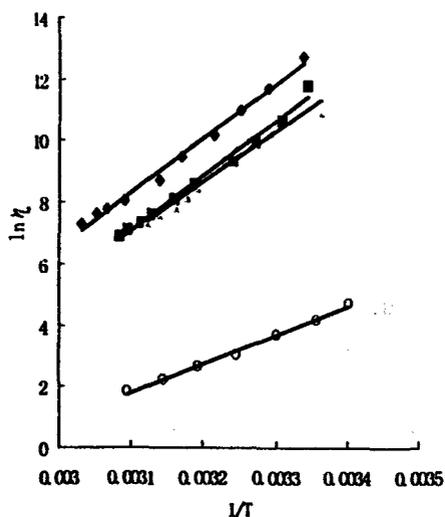


Fig. 1 The relation of viscosity and temperature

- ◆ PAAS (BTDA/PMDA; 75/25)/ODA-TEA
- ▲ PAAS (BTDA/PMDA; 50/50)/ODA-TEA
- BTDA/ODA-TEA
- PMDA/ODA-DMEA

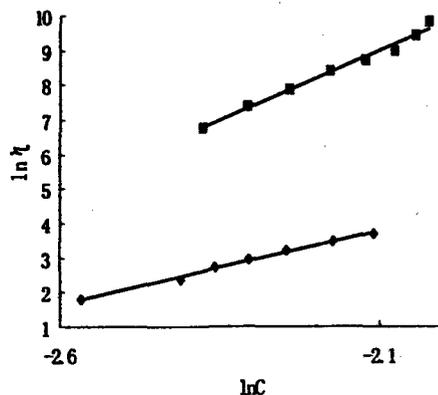


Fig. 2 The relation of concentration and viscosity

- ◆ PMDA/ODA-DMEA
- BTDA/ODA-TEA

We used a mixed solvent of THF and MeOH instead of DMAc for obtaining PAA film without any imide structure. This was proved by IR spectrum of the PAA film prepared from THF/MeOH PAA solution since we did not find absorption band near 1778cm^{-1} indicating the imide structure. This absorption peak appeared in IR by heating treatment until 250°C in Fig.3. IR spectrum of PAA salts prepared from BTDA/ODA was shown in Fig.3-b. We did not find absorption at either 1778cm^{-1} or 1720cm^{-1} which stands for the polyimide and poly(amide acid) structures respectively, but the absorption at 1400cm^{-1} which corresponds to carboxylate anion was observed. The structures of the PAA salts (PMDA/ODA-TEA) were confirmed by $^1\text{H-NMR}$, the result was the same that had been reported by Echigo (Fig.4) There were cis- and trans- isomers in PAA salt. We found DMSO solution of PAA salt became muddiness by heating at 160°C for 30 minutes and observed the peaks at 7.94, 7.98 and 8.06 ppm disappeared (Fig.4-a). But a new peak at 9.0 ppm was observed. It corresponds proton of carboxylic acid (Fig.4-b). After a heating treatment at 250°C , IR spectrum became the same as that of the corresponding polyimide. They all were imidized by decomposition of PAA salt followed by cyclization. At the same time, we observed the heating process by DSC and TGA and found there was an endothermal peak at $150\text{--}162^\circ\text{C}$ in DSC. It indicated that the salts were decomposed by Hoffmann reaction and formed cyclization at the same time. This was further confirmed by IR (after heating at 160°C). It has been known that the imidization mechanism of PAA salt was different from that of PAA (endothermal peak at 182°C) by DSC and TGA (Fig.5) measurement.

We found the polyimide film whose thickness more than $10\ \mu\text{m}$ cannot be obtained with PAA deriving from PMDA/ODA or BTDA/ODA salts (TEA and DMEA) in water solutions. After thermal treatment the film cracked. In order to prove whether the residual water inside PAA salt film affects the strength of the polyimide film, we prepared PAA TEA salt in MeOH solution for comparison. Because PAA DMEA salt was insoluble in MeOH, the viscosity of salt in MeOH was lower than that of water

solution. The result of film formation from MeOH was the same as the water solution. The crack still occurred in film after imidization. Therefore the reason of crack was independent of water. It is assumed that crack occurs due to the internal stress generated during the thermal treatment. The polyimide film can be obtained in a several micron meter thickness. We think the internal stress is low during imidization. However, we found the inflation of film at 160°C and shrinkage occurred. This was a reason which generates internal stress. The strength of film made from BTDA/ODA was better than that of PMDA/ODA. According to the above result, we can apply PAA salt in water solution for heat resistant coating industry. It can be blended with other water coating, e.g., fluorine containing latexes.

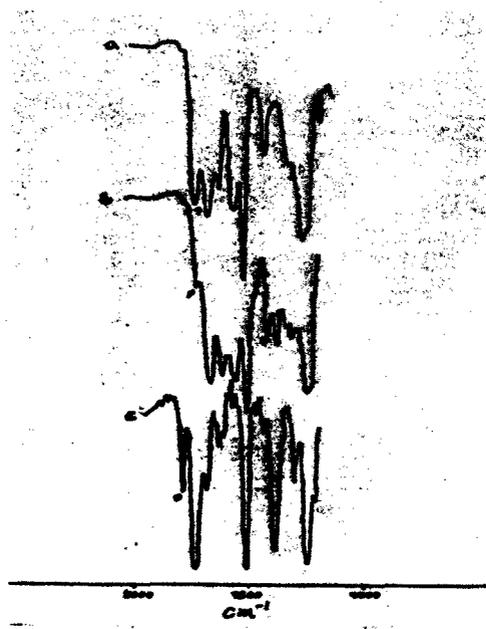


Fig.3 IR spectrum. a. PAA; b. PAAS; c. PI

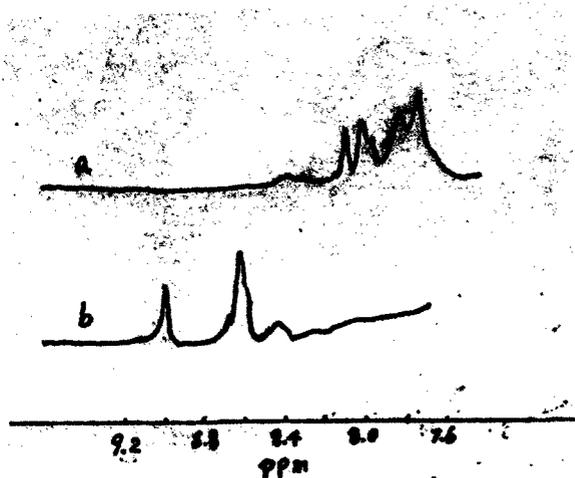


Fig. 4 NMR spectrum. of PAAS (PMDA/ODA-TEA)

a. Room temperature; b. 160°C for 30 min.

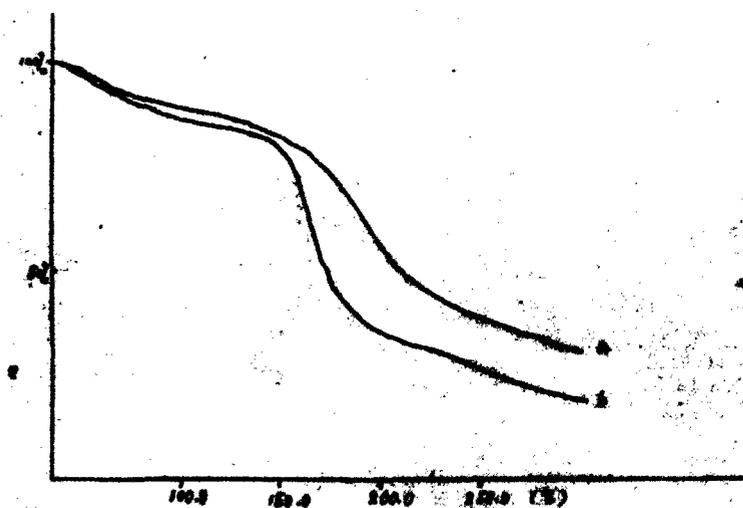


Fig. 5 DSC of PAA and PAAS at 10°C in air.

a. PAA(PMDA/ODA); b. PAAS(PMDA/ODA-TEA)

Conclusion

PAA salts and their water, MeOH solutions were prepared. And the structures of salts were characterized by IR and NMR. We studied the heating imidization by DSC and TGA. The properties of water solutions were measured under various temperatures and concentrations. A thicker polyimide film can be obtained in water or MeOH solution with heat imidization. It can be applied for heat resistant coating industry.

References

1. C.E.Sroog, J. Polym. Sci., Macromol. Rev., **11**, 161 (1976).
2. H.J.Merrem, R.Klug, and J. Hartner, Polyimide: Synthesis, Characterization and Applications, K.L. Mittal, Ed., Plenum Press, New York, 1980, p.919.
3. N. Yoda and H Hiramoto, J. Macromol. Sci. Chem., **A21**, 1641 (1984).
4. S. Kubota, T. Moriwaki, T. Ando, and A. Fukami, J. Appl. Polym. Sci., **33**, 1763 (1987).
5. W. Volksen, D. Y. Yoon, J. L. Hedrick, and D. Hofer, in Materials Science of High Temperature Polymers for Microelectronics, MRS Symposia Proceedings, Materials Res. Soc., Pittsburgh, Pa., 1991, Vol. 227, p.23
6. J. A. Kreuz, A. L. Endrey, F. P. Gay, and C. E. Sroog, J. Polym. Sci., Part A: Polym. Chem., **4**, 2607 (1966).
7. U.S.P 4600770 (1986).
8. U.S.P 4480088 (1984).
9. U.S.P 4428977 (1984).
10. U.S.P 4418190 (1983).
11. Y. Echigo, N. Miki, and I. Tomioka, J. Polym. Sci., Part A: Polym. Chem., Vol.35, 2493 (1997).
12. Q. Li, T. Yamashita, K. Horie, H. Yoshimoto, and T. Miwa, J. Polym. Sci., Part A: Polym. Chem., Vol.36, 1329 (1998).