A mechanism describing polyamic acid solution viscosity change on storage at high temperature

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The storage of polyamic acid solution at high temperature is known to bring about a decrease in solution viscosity. This paper describes an investigation of a factor of this viscosity change at 80°C for polyamic acid solution derived from 3,3',4,4'-biphenyltetracarboxylic acid dianhydride and *p*-phenylene diamine in *N*-methyl-2-pyrrolidone. This reduction of viscosity was caused by a weight-average molecular weight reduction. The relationship between weight-average molecular weight measured by a light scattering method and 10 wt% solution viscosity, η, at 25°C could be described as $\eta = 4.29 \times 10^{-17} M^{3.35}$.

(Keywords: polyamic acid; viscosity; temperature effect; molecular weight; light scattering)

INTRODUCTION

In electronics applications polyimide films have been widely used as an insulation layer[1], but the discovery of low thermal expansion polyimides[2,3] showed their even greater usefulness. Several studies on applications of low thermal expansion polyimides in multi-layer wiring for VLSIs and high-density multi-layer interconnections have demonstrated utilization possibilities[4,5]. To get a planar insulating layer with low thermal stress, high solid content polyamic acid solutions which give low thermal expansion polyimides are desired. As concentration of polyamic acid is limited by its viscosity, many successive efforts to obtain lower viscosity solutions using monomeric and/or oligomeric species with terminal groups such as esters[6], maleimides[7] and ethnyl[8] functionalities have been reported. On the other hand, heat treatment of polyamic acid solutions has also been reported as a viscosity control technique[9]. Although many studies concerning instability of polyamic acid solution viscosity on storing at ambient or refrigeration temperature have elucidated that molecular weight reduction and/or chain length equilibrium of the solution contribute to this instability[10,11], little work has been done dealing with the thermal treatment of polyamic acid.

So as a part of our ongoing series of studies on low thermal expansion polyimides, a mechanism of polyamic acid solution viscosity change on storage at 80°C was investigated. The weight-average molecular weights which were measured by a light scattering method, were correlated with solution viscosity.

EXPERIMENTAL

Reagent

N-methyl-2-pyrrolidone (*N*MP; 99% purity grade; b.p. 204°C), was purchased from Tokyo Ohka Kogyo Co. Ltd and used as received. 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) was purchased from Yuki Gosei Kogyo Co. Ltd and heated at 200°C for 2 h just before use to convert all carboxyl groups into anhydride. The anhydride melting point was 292°C. *p*-phenylene diamine(*p*-PDA; 98% purity grade) was purchased from Tokyo Kasei Kogyo Co. Ltd and purified by sublimation. The melting point was 145°C.

Sample preparation

Polyamic acid solution was prepared in a closed vessel at ambient temperature under a nitrogen atmosphere at a concentration of 10% (w/w) solids in *N*MP. The s-BPDA was added to an equimolar amount of *p*-PDA dissolved in *N*MP. After the increase in solution viscosity stopped at 22.75 Pa·s, the solution was heated at 80°C until the decrease in solution viscosity stopped at 0.64 Pa·s. During this thermal treatment some portions of the solution were withdrawn at intervals of 0.5–1 h. These polyamic acid samples were refrigerated.

Polyamic acids having weight-average molecular weights 13 900, 19 500, 29 000, 37 100 and 61 000 were prepared using one functional monomer phthalic anhydride instead of some part of the s-BPDA amount to control the $\bar{M}_w$. Except for heat treatment, preparation and storage procedures were as described above.

Measurements

Viscosity. All viscosities were measured at 25°C in *N*MP solutions. Intrinsic viscosities were measured by a Cannon-Manning semi-microviscometer with solvent flow time of 124.3 s. The viscosities of 10 wt% solutions were measured by a cone plate type viscometer (Tokyo Keiki Co. Ltd Viscinic EMD).

Light scattering. For a Zimm-plot 0.6–0.05 wt% *N*MP solutions were prepared and filtered with a 0.2 μm pore size membrane filter. These solutions had no absorption at a light scattering enhancement length wave of 632.8 nm. In dilute solutions ($c < 0.1$ wt%) a significant effect from

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dissociation of polyamic acid was observed[12], so measurements were carried out on 0.6–0.2 wt% concentration solutions. The scattering was measured at 14 points ranging from 30° to 140° using a modified Photal DLS700 to cut fluorescence by band pass filter. The solutions of 0.3 wt% in *N*MP were prepared for one concentration method[13] and scattering was measured at the same angles as the Zimm-plot.

Refractive index of *N*MP at 632.8 nm 1.4655 was calculated according to Kamata[14] from $n_D = 1.4682$ and correction factor θ using equation (1).

$$[n_{632.6} - n_D = -0.01059 + 0.0001981\theta] \qquad (1)$$

The increment of refractive index due to polymer concentration was 0.1999 (ml mg^{-1}). Differences in the value between polymer samples were negligibly small.

Infra-red spectroscopic analysis. Infra-red spectra of polymers were measured by the Hitachi 260-50 model using KBr discs. The solid polymer samples were prepared by reprecipitation in water from 3 wt% polymer solution in *N*MP and dried for 12 h in vacuo at 60°C.

RESULTS AND DISCUSSION

The viscosity change of s-BPDA/*p*-PDA polyamic acid solution at 80 ± 2°C was investigated, as shown in *Figure 1*. The decrease in solution viscosity was rapid at first and slowed down and stopped after 50 h.

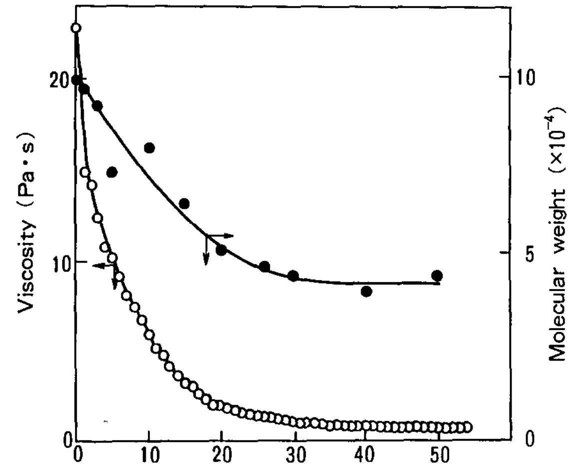

Figure 1 Viscosity and molecular weight change of s-BPDA/*p*-PDA polyamic acid solution in *N*MP/10 wt%

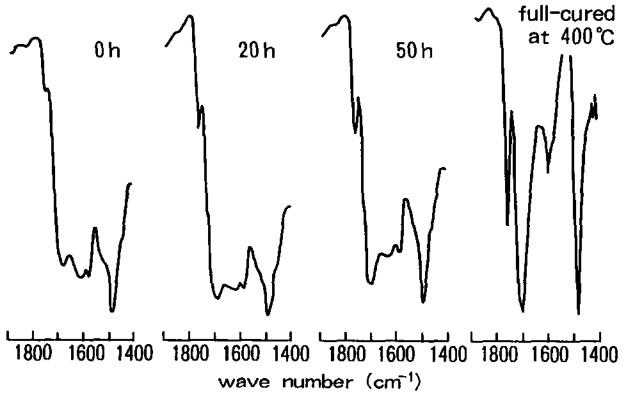

Figure 2 Infrared spectrum change of s-BPDA/*p*-PDA polyamic acid by heat treatment at 80°C

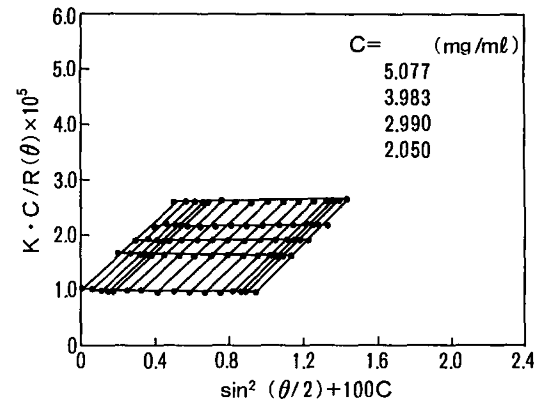

Figure 3 Zimm-plot of s-BPDA/*p*-PDA polyamic acid without heat treatment at 80°C for 20 h

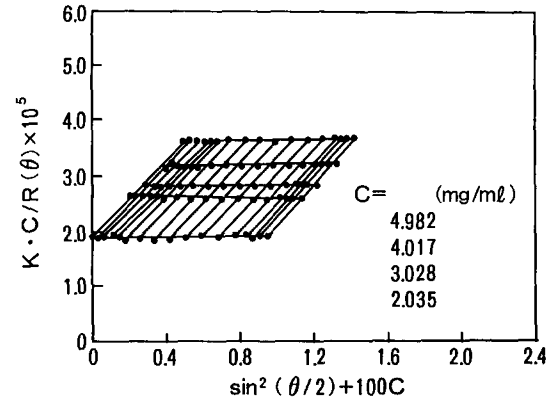

Figure 4 Zimm-plot of s-BPDA/*p*-PDA polyamic acid after heating at 80°C for 20 h

The infra-red spectra of polymers after heat treatment for 0, 20, 50 h at 80°C, and a spectrum of fully cured polyimide at 400°C, are reproduced in *Figure 2*. The intensity of the absorption at 1770 cm^{-1}, which is attributed to the imide bond, increased with heating time. The imide ring and two aromatic rings linked by it are placed in a straight line[15] and the structure of polyimide, based on s-BPDA and *p*-PDA, is rodlike[3]. An increase in solution viscosity with imidization reaction would be expected, if the imidization reaction was the dominant factor in the solution viscosity change. So the imidization reaction should not be the main factor for this decrease in viscosity.

The Zimm-plots of three samples with different viscosities are shown in *Figure 3–5*. *Figure 3* plots results of the sample without heat treatment. *Figures 4* and *5* are the results of samples which have been heated at 80°C for 20 h and 50 h, respectively. The results could be connected by straight extrapolated lines, indicating that they were free from dissociation effects. The light scattering results and inherent viscosities of those samples are shown in *Table 1*. Degradation of $\bar{M}_w$ was clearly apparent. Values of the second virial coefficients A_2 of the three samples ($2.05–1.52 \times 10^{-3}$) indicated that *N*MP was a good solvent for the polymer, as was also found for other polyamic acids[12]. Considering that the polymer chain was comprised of rodlike segments with length l_0 of 1.7 nm as shown in *Figure 6*, radii of gyration $\langle S^2 \rangle^{1/2}$ in *Table 1* were rather small. Presistent length *A* of No. 1 which was calculated from $\langle S^2 \rangle^{1/2}$, l_0 and the degree of

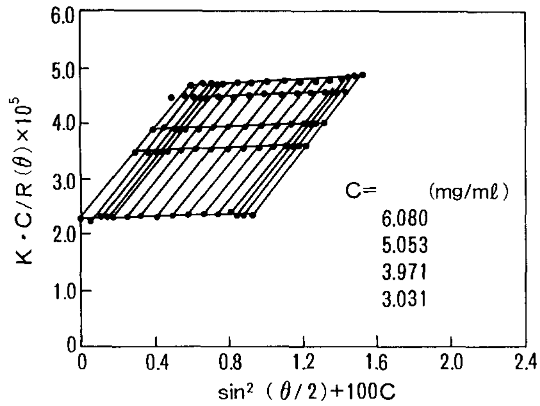

Figure 5 Zimm-plot of s-BPDA/*p*-PDA polyamic acid after heating at 80°C for 50 h

Table 1 Dilute solution properties of s-BPDA/*p*-PDA polyamic acid solution in *N*MP

No.	$\bar{M}_w \times 10^{-4}$ (g mol^{-1})	$A_2 \times 10^3$	$\langle S^2 \rangle^{1/2}$ (nm)	[η] (ml g^{-1})
1	9.97	1.52	16.8	1.10
7	5.31	1.65	14.6	0.72
11	4.54	2.05	12.2	0.61

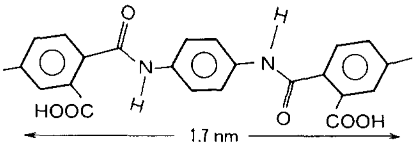

Figure 6 Structure of rigid segment of s-BPDA/*p*-PDA polyamic acid

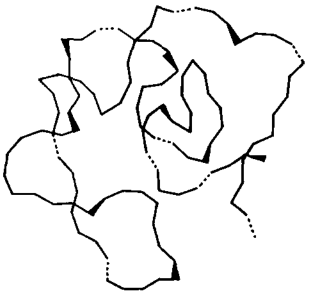

Figure 7 Schematic representation of s-BPDA/*p*-PDA polyamic acid solution with $N = 100$, $l_0 = 1.7$ nm, $A = 4.0$ nm

polymerization *N* using equation (2) was only 2.3 times that of l_0.

$$[\langle S^2 \rangle^{1/2} = \sqrt{(N \cdot A \cdot l_0/6)}] \qquad (2)$$

This result suggested that the polymer chain was flexible in *N*MP. This flexibility should be caused by the positional isomer of the products of anhydride ring opening[16]. Three positional isomers in which two amide groups are in 4,4′-, 3,4′-, 3,3′-, positions of biphenyl group respectively are expected. Also, the zigzag structure of 3,4′-, 3,3′-, isomer should introduce flexibility to the polymer chain. A schematic representation of the system with a hypothetical chain of $N = 100$, $l_0 = 1.7$ nm is shown in *Figure 7*.

The values of $\bar{M}_w$ of the other samples were calculated by the one concentration method. The samples were too concentrated to calculate molecular weight without correction, so A_2 obtained from interpolation of the A_2 values of the three samples in *Table 1* were used for the correction. The calculated weight-average molecular weights are shown in *Figure 1*. A correlation could be seen between η and $\bar{M}_w$. If the molecular weight degradation played an important role in the solution viscosity change, the relationship between $\bar{M}_w$ and η could be described with equation (3)[17].

$$\eta \propto M^a \qquad (3)$$

The results of log η − log $\bar{M}_w$ plot for with and without heat treated polyamic acid solutions are shown in *Figure 8*. As the plots of heat treated samples gave a straight line with slope equal to 3.35, the polyamic acid solution viscosity change on storage at high temperatures should be caused by molecular weight degradation. The difference in slopes between with and without heat treated samples was small, so effects of the imidization reaction to viscosities might be negligibly small. Though the cause of the viscosity difference between the two kinds of samples, heat treated and untreated, was not clear, a more complicated interaction characteristic of a high concentration region, such as entanglement of polymer chains, may contribute to this phenomenon.

CONCLUSIONS

Viscosity change of polyamic acid derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) and *p*-phenylene diamine (*p*-PDA) solution at 80°C was investigated. This viscosity change was caused by a weight-average molecular weight reduction. The relationship between weight-average molecular weight and 10 wt% solution viscosity at 25°C could be described as $\eta = 4.29 \times$

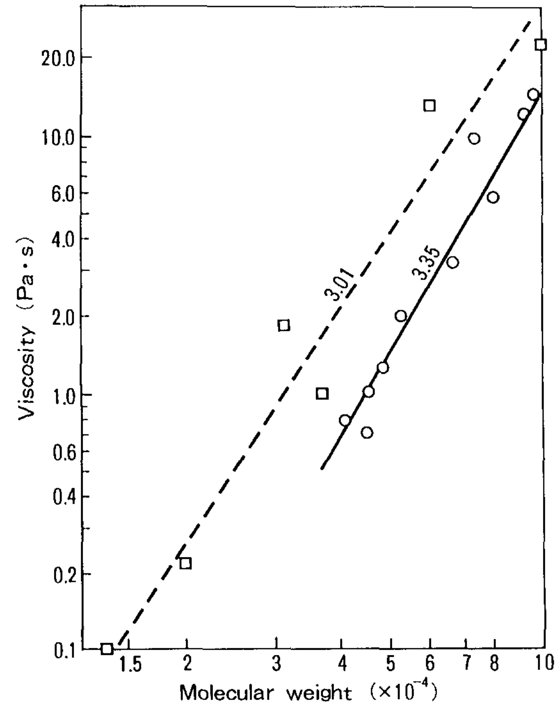

Figure 8 Molecular weight power dependency of the viscosity of polyamic acid solutions in *N*MP/10 wt%, with heat treatment (○) and without heat treatment (□) at 80°C

$10^{-17}M^{3.35}$. The persistance length of a polymer chain without heat treatment was 2.3 times that of the rodlike segment, and was characteristic of moderately extended coils as expected from molecular structure.

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