BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3587—3588 (1973)

Torsional Braid Analysis of Magnesium Highpolyphosphate Coacervates

Takao UMEGAKI and Takafumi KANAZAWA
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

(Received November 15, 1972)

Magnesium highpolyphosphate (MP) solutions with high viscosity (10—10^3 poise) and transparency were prepared by coacervation from mixed solutions of sodium highpolyphosphate and $MgCl_2$ under appropriate conditions.[1]

The physicochemical properties of alkali salts of highpolyphosphate have been described in detail by many researchers, but not those of other metal salts. Thermal changes of MP coacervates at temperatures from room temperature to about 1000 °C were examined by means of DTA, TGA and high temperature X-ray diffraction technique as a part of studies on non-alkali condensed phosphates.[2,3]

The present paper deals with temperature dependence of visco-elasticity of magnesium highpolyphosphate obtained by coacervation. Phase transition, thermal degradation and some other thermal changes of the MP at temperatures, from −120 to +80 °C were discussed on the basis of measurements of relative rigidity and logarithmic decrement by a torsional braid analyzer.

Experimental

Preparation of Magnesium Highpolyphosphate Coacervates. A 20% $MgCl_2$ solution (139 parts) was poured into a 15% solution (400 parts) of sodium methaphosphate (both guaranteed reagents of Kanto Chemical Co., Inc.) at room temperature. A white and opaque coacervate was obtained when ethyl alcohol was added to the well-stirred mixture of the two solutions. Addition of alcohol was continued until the coacervate no longer formed in clear liquid phase of the mixture. The MP coacervate (Sample I) was then accumulated by decantation.

Another MP coacervate (Sample II) was prepared by addition of distilled water to Sample I, in a ratio of 1 : 1 in weight. The chemical compositions of the two coacervates used are shown in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF MAGNESIUM HIGHPOLYPHOSPHATE COACERVATES

Coacervate	Contents (%)			
	MgO	P_2O_5	Na_2O	H_2O
Sample I	6.8	36.8	4.1	52.9
Sample II	3.4	18.2	2.1	76.4

Measurement of Damped Oscillation. Magnesium coacervates settled in a week after preparation, the white, opaque coacervates becoming transparent. The samples were made to adhere to strips of glass cloth. The composite specimen of coacervate and glass cloth was suspended in a torsional pendulum type visco-elastometer (type RD-100, Applied Electric Laboratory, Ohyo Denki Kenkyujo Ltd.). For the experiments at low temperatures, liquid nitrogen was introduced into the visco-elastometer evacuated in advance and passed over the specimen. Damped oscillation was initiated manually at the desired temperature and recorded with a pen-writing oscillograph.

Calculation of Logarithmic Decrement and Relative Rigidity. Logarithmic decrement α_T and relative rigidity G_r were calculated as follows:[4]

$$\alpha_T = \ln A_n/A_{n+1}, \qquad G_r = (P_0/P_1)^2$$

where A_n is the n-th amplitude of damped sine wave, and P_0 and P_1 are periods of the oscillations of MP coacervate sample at temperatures T_0 and T_1, respectively. A certain period P_0 is fixed as a standard.

Results and Discussion

The thermomechanical spectra for MP coacervates are given in Figs. 1 and 2. No change in the logarithmic decrement and relative rigidity for Sample I was found over a temperature range between −120 and −60 °C, the solid phase of MP coacervate being retained without any thermal transformation. Relative rigidity for Sample I (Fig. 1) decreased with temperature rise, the lowering of the rigidity in the vicinity of 0 °C being remarkable. An inflection point of rigidity-temperature curve was found between 20 and 30 °C.

In this type of dynamic experiment the logarithmic decrement is directly related to the phase angle between the stress and strain, providing a measure of the mechanical energy dissipated per cycle compared with

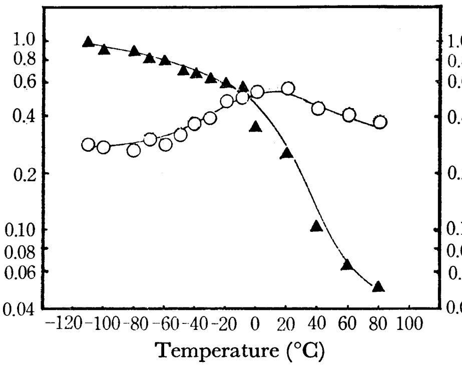

Fig. 1. TBA of sample I.
▲: G_r (relative rigidity), ○: α_T (logarithmic decrement)

---

[1] T. Kanazawa, H. Kawazoe, and T. Matsubara, *Kogyo Kagaku Zasshi*, **74**, 1784 (1971).

[2] T. Kanazawa, T. Umegaki, and H. Kawazoe, *Asahi Garasu Kogyo Gijyutsu Shoreikai Kenkyu Hokoku*, **21**, 81 (1972).

[3] T. Kanazawa, T. Umegaki, and Y. Nakayama, Preprint of Lectures at the 26th Annual Meeting of the Chemical Society of Japan, II, p. 687 (1972).

[4] J. K. Gillham, *Appl. Polym. Symp.*, No. 2, 45 (1966).

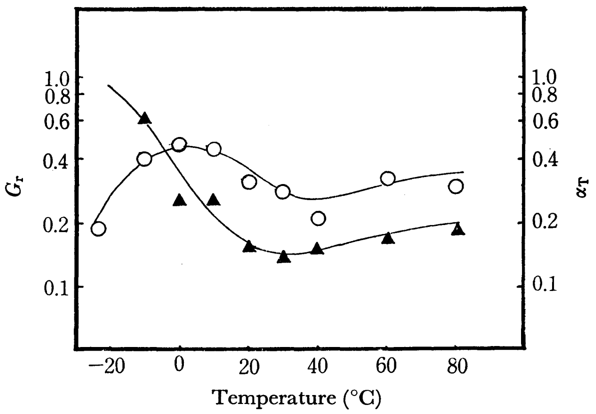

Fig. 2. TBA of Sample II.
▲: G_r (relative rigidity), ○: α_T (logarithmic decrement).

that recovered.[4] At the temperature of the peak for the decrement the MP coacervate was believed to be in the most random state of anion chains of the phosphate polymer.

It seems that the peak of logarithmic decrement and the drastic decrease of relative rigidity between 0 and 60 °C indicate melting of the MP coacervate.

Owing to the wide distribution in the chain length of polyphosphate ions, the peak of the decrement (Fig. 1) is broadened, which is almost unavoidable on the wet preparation of magnesium polyphosphates.

The maximum value of logarithmic decrement and the inflection point in rigidity-temperature curve shift to lower temperature compared with those of Sample I (Fig. 2). The thermomechanical behavior in the vicinity of 0 °C suggests melting of Sample II as well as Sample I. The gradual increase in rigidity and the decrement above 40 °C indicate stiffening of the specimen. Probably magnesium polyphosphates in water-rich coacervate are easily concentrated by vaporization of water, as compared with Sample I with lower content of water.

Besides the concentration of the polyphosphates, the above increase may be explained in terms of partial crystallization of orthophosphates formed in the course of thermal degradation of polyphosphates. However, a temperature of about 40 °C is believed to be somewhat low for initiation of the degradation.

The thermomechanical properties of the MP coacervates were described over a temperature range from −120 to +80 °C. Both coacervates settled in a week and the change of visco-elasticity with time was not examined. It is necessary to measure the time dependence of the rigidity and the decrement under controlled vapor pressure.

This work was supported by a grant from the Asahi Glass Foundation for Contribution to Industrial Technology, for which the authors wish to express their sincere appreciation. Thanks are due to Mr. Nobuhiro Sasaki, Manager of Technical Division, Applied Electric Laboratory (Ohyo Denki Kenkyujo), Ltd. for cooperation in the measurement of visco-elasticity.