

# DYNAMIC VISCOELASTICITY AND SPINNING BEHAVIOR OF AN ORGANOGELATOR, PMDA-R, DISSOLVED IN VARIOUS OILS

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## ABSTRACT

We synthesized a low-molecular-mass organogelator, pyromellitimides (PMDA-R),<sup>1</sup> which is composed of four amide groups with two kinds of side chains (R and R'). We evaluated the effects of compounds with one side chain on 2-ethylhexyl or oleyl and those of the other side chain systematically modified on the rheological properties of compounds dissolved in paraffin oil and three kinds of ester oils as solvents. For the application of such additives in cosmetics, paints, etc., it is necessary to obtain not only the viscosity and viscoelasticity data, but also spinning characteristics such as thread pulling and thread breakage. We used a prototyped spinnability measuring device<sup>2</sup> to classify the threading patterns of the samples and organize them in relation to the viscoelasticity of the fluid. We also observed transmission electron microscopy (TEM) images that may be related to the degree of crystallinity of compounds.

## RESULTS AND DISCUSSION

Figure 1 shows the results of different concentrations of PMDA-C<sub>6</sub>/oleyl in isododecane. Figure 1(a) shows the steady-state flow characteristics. Although not shown in the figure, the viscosity of isododecane remained constant at 1.4 mPa·s independent of the shear rate. Open shapes in the figure indicate viscosity, and closed shapes indicate the first normal stress difference. The addition of 1 wt% caused a viscosity increase by one order, showing an almost constant value in the low-shear-rate range (up to  $\dot{\gamma} = 14.7 \text{ s}^{-1}$ ), which is considered to correspond to a plateau region. At shear rates above  $14.7 \text{ s}^{-1}$ , the viscosity gradually increased with decreasing shear rate, down to 2.9 mPa·s at  $1000 \text{ s}^{-1}$ . At 0.3 wt%, the viscosity value increased by approximately two orders of magnitude compared to the solvent, up to a shear rate of  $1.47 \text{ s}^{-1}$ , and the viscosity gradually decreased at higher shear rates. The increasing viscosity effect in the low-shear-rate range became more pronounced with increasing additive concentration, and a tendency to exhibit shear thinning was apparent in the low-shear-rate range as the concentration increased. Here, the value of the first normal stress difference was negative for all regions measured at 0.1 wt%, but at 0.3 wt%, two-order values were observed at high shear

rates, and three-digit values were observed thereafter. Figure 1(b) shows the dynamic viscoelastic moduli. At the low concentrations of 0.1 and 0.3 wt%,  $G'$  and  $G''$  were proportional to the square and first power of  $\omega$ , respectively, and their positional relationship was reversed as  $\omega$  increased. At 0.5 wt% or more, a similar phenomenon was observed at low frequencies, and with increasing concentration. Both  $G'$  and  $G''$  increased with increasing concentration while the intersection hardly changed position.

On the other hand, the reciprocal of  $\omega$  at the intersection point is the relaxation time of the sample, and this result indicates that the relaxation times of the samples are almost the same regardless of the concentration.

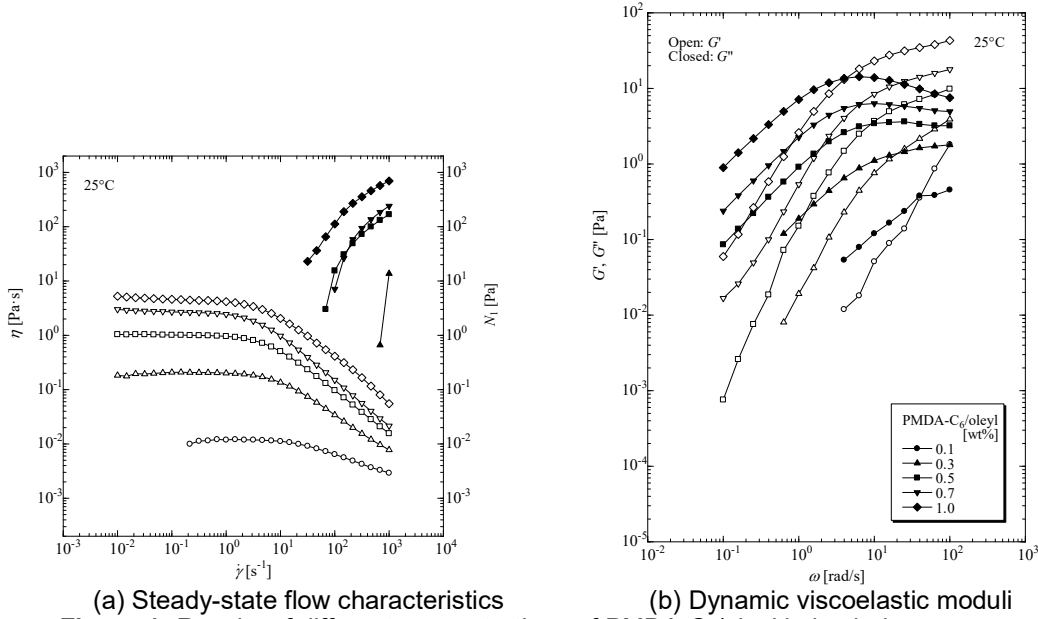


Figure 2(a) shows the results of the stringiness test. Spinnability was observed from a sample with an added concentration of 0.5 wt% in the device used in this experiment. The rod in contact with the liquid surface of the sample rises as if pulling the sample, increasing the stress. Then, after the stress reaches maximum value, it takes on a thread-like shape, and the thread gradually becomes thinner until it finally breaks. Since the thread remained present even when stress was below 0, we used the data up to the length at which the thread broke, which we measured from video footage. According to the figure, if the lifting speed is the same, the gradient corresponding to the part where the liquid surface rises is almost the same, so we can consider that the lifting force of the sample is almost the same at an addition concentration of 0.5 wt% or more. At 0.5 wt%, the maximum stress was 0.67 N and the string length was 4 mm. At 0.7 wt%, there is a portion where the gradient changes until the thread breaks, and the inflection point is approximately 6 mm. This trend was also seen at 1.0 wt%. The maximum stresses at 0.7 and 1.0 wt% were 1.2 and 2.2 mN, respectively, and the spinning lengths were 9.7 and 19.3 mm. This is simply the result that, when the concentration of the additive increases and the viscosity and viscoelasticity of the sample increase, spinning becomes apparent and the maximum spinning stress and length increase.

For this reason, the maximum value of the spinning stress is standardized to 1 and the maximum spinning length is 1. The results are shown in Fig. 2(b). Focusing on the upward

convex part, the shape is almost line-symmetrical around the maximum stress value at any concentration, but at 0.7 and 1.0 wt%, the tail spreads until the thread breaks and there is also a distortion in the symmetry. The process from the emergence of spinning to breakage is expressed after the maximum stress, and it can be clearly seen that the higher the concentration of the additive, the longer the period after the stress drops below 0.

In addition, we plan to report on the effects of changing the side chain.

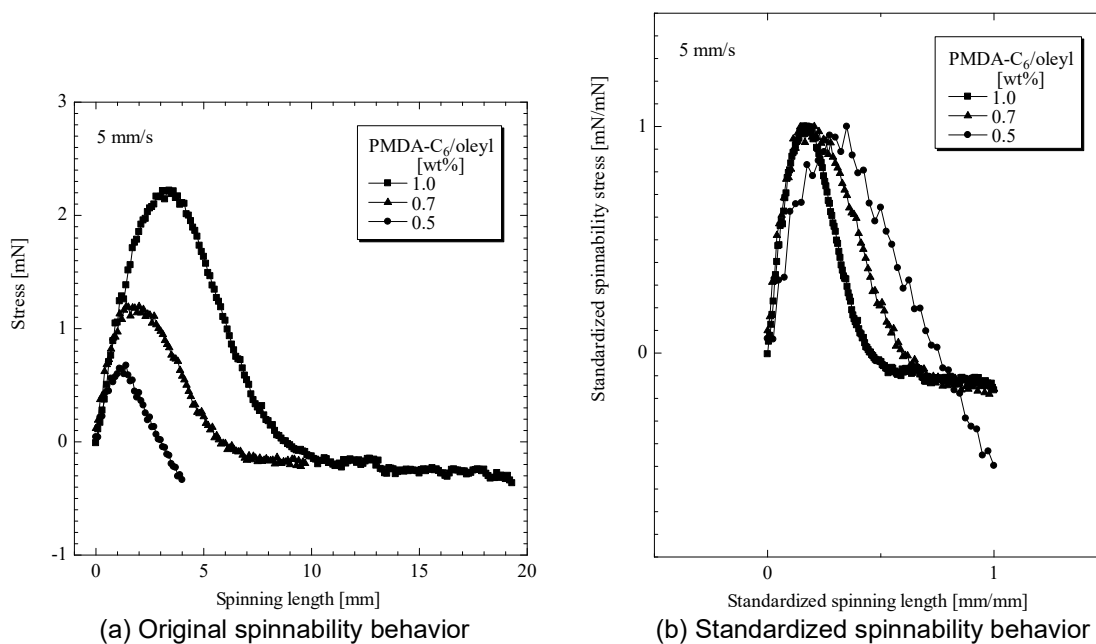


Figure 2: Spinnability of PMDA-C<sub>6</sub>/oleyl in isododecane

## ACKNOWLEDGEMENTS

The authors wish to thank Dr. Y. Sakanishi (Taiyo Kagaku Co., Ltd.) for the synthesized PMDA-R compounds. This research was supported by JSPS KAKENHI, Grant-in-Aid for Young Scientists, 2020-2022 (JP20K15076, Aya Kaide) and Grant-in-Aid for Scientific Research (C), 2022-2025 (JP22K04805, Aya Kaide).

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