

Rheological Properties and Self-Assembled Structures of Newly Synthesized Amide Organogelators, Butane 1,2,3,4-Tetracarboxamides, in Isododecane

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Abstract

The objectives of this study were to develop organogelators suitable for industrial use and to probe the viscosity-increasing mechanisms of such organic compounds. Butane 1,2,3,4-tetracarboxamides, new organogelators that each has four chemical side chains, were synthesized. Two oleyl groups, each with another two side chains that varied from C4 to C18, were introduced to control the solubility and crystallinity of the compounds, and their solubility and rheological properties in isododecane were evaluated. The rheological properties of different amide compounds, N,N',N'',N'''-1,2,4,5-tetra alkyl/alkenyl pyromellitimides with the same four chemical side chains, were also obtained to consider the skeleton's effect on self-assembled structures due to hydrogen bonding among amide groups. The viscosity-increasing mechanism of the compounds was discussed through linkage of the molecular design, rheological evaluation, and morphological observations in this paper.

Keywords

Organic Compounds, Chemical Synthesis, Viscoelastic Property, Transmission Electron Microscope (TEM), Self-Assembled Structure

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1. Introduction

Viscosity control for hydrophobic fluids (oils) is necessary in a wide range of industrial applications and commercial goods, such as inks, paints, cosmetics, pharmaceutical products, and petroleum products.

Viscosity control agents for organic solvents (organogelators) have been developed widely over the past decade within the field of hydrophobic-supramolecular materials [1]-[10]. In such situations, low-molecular-weight organogelators constructed from aromatic rings have been reported, e.g., with a biphenyl structure [11] and bisurea compounds [12]. Skeleton structures of benzene or cyclohexane with chemical side chains have also been reported as organogelators, the thickening properties of which may be related to the hydrogen bonds of the amide groups [13] [14]. On the other hand, the solubility of such organogelators may influence chemical side chains [15]. We reported on the versatility of seven commercially available organogelators for several organic solvents (oils) together with our newly synthesized organogelators, each having four alkyl chains to the aromatic ring 3,3',4,4'-benzophenone tetracarboxamides [15]. We also synthesized and examined compounds with benzene as a skeleton having four alkyl chains: N,N',N'',N'''-1,2,4,5-tetra alkyl/alkenyl pyromellitimides (PMDA) [15]; the results suggested that controlling the solubility and crystallinity of compounds is key to realizing appropriate organogelators.

In this paper, we continue our research by using nonaromatic compounds, which are thought to be safer for commercial products. New organogelators, butane 1,2,3,4-tetracarboxamides, each with four chemical side chains, were synthesized by introducing two oleyl groups with another two side chains, which varied from C4 to C18. Since isododecane is widely used as a hydrophobic solvent for cosmetic and sanitary products, we selected isododecane as a test fluid in this study. The rheological property of PMDA was also evaluated to consider the influence of the skeleton. The viscosity-increasing properties of the compounds were evaluated not only by measuring their rheological properties but also by observing their morphologies using a transmission electron microscope (TEM), which can probe the self-assembled structures of compound molecules.

2. Experimental

2.1. Synthesis of the Organogelators and Preparation of Solutions

The chemical structure of the newly synthesized organogelators is that of butane 1,2,3,4-tetracarboxamide, as shown in **Figure 1**. The chemical side chain R was fixed as oleyl and the side chain R' was varied as shown in **Table 1** (compounds **1** - **7**). The method of synthesizing compound **5** is described in detail as an example:

Oleyl amine (11.3 g, 42 mmol) was added dropwise to a stirred slurry of butane 1,2,3,4-tetracarboxylic dianhydride (4.2 g, 21 mmol) and pyridine (20 ml) under nitrogen gas at 50°C. After the mixture was stirred for 3 h to give a homogeneous solution, diisopropylcarbodiimide (5.8 g, 48 mmol) and 2-ethylhexyl amine (5.4 g, 42 mmol) were added and the solution was stirred for 8 h. The solvent was removed *in vacuo* to give the crude product as a yellow gel-like material. This material was washed with methanol, and the resultant product was filtered to give compound **5**.

The hydrophobic solvent used in this study was isododecane (Maruzen Petrochemical Co., Tokyo, Japan) without further purification. The synthesized compounds were carefully dissolved in the solvent under agitation for 12 h at 100°C - 120°C.

Table 1. Chemical side chains (R') and compound number.

Compound No.	R'
1	n-C ₁₈ H ₃₇
2	n-C ₁₄ H ₂₉
3	n-C ₁₂ H ₂₅
4	n-C ₁₀ H ₂₁
5	2-Ethylhexyl
6	n-C ₆ H ₁₃
7	n-C ₄ H ₉

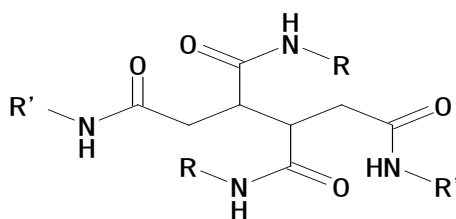


Figure 1. Chemical structure of butane 1,2,3,4-tetracarboxamide.

2.2. Solubility and Rheological Measurements

The solubility of the synthesized compounds to isododecane was assessed by both visual observation and quantitative evaluation of absorbance at an absorption wavelength in the vicinity of 660 nm, measured by an ultraviolet-visible spectrophotometer (UVmini1240, Shimadzu Corporation, Kyoto, Japan).

Rheological properties were measured using a cone and plate rheometer (NRM-2000R, Elquest Corporation, Chiba, Japan). The diameter and angle of the cone were 17.1 mm and 3°, respectively. The equilibrium flow property was measured for the shear rate range from 0.01 - 500 s⁻¹. The dynamic viscoelastic property was evaluated by the method of forced oscillation [16]. In this method, the viscoelasticity at each frequency is analyzed according to the Maxwell model, which consists of a spring and a dashpot in a series. When a sinusoidal strain is imposed upon a sample, sinusoidal stress will result at the same frequency at a phase-shift defined by the angle δ . The complex viscoelastic modulus G^* is then defined as the ratio of the stress and strain amplitude. The stress-strain relation may be represented as having a component that is in phase with the strain and a component that is 90° out of phase with the strain. The former represents elasticity, which is defined as the storage modulus G' (Pa), while the latter is the loss modulus G'' (Pa). These relations can be represented by the following equations:

$$G' = G^* \cos \delta \quad (1)$$

$$G'' = G^* \sin \delta \quad (2)$$

The measurements were conducted at a strain of 0.1 with varying angular velocity ω of sine wave oscillation from 0.06 - 63 rad/s. At the same time, the strain dependence of the sample's viscoelasticity was also measured at a frequency of 1.0 Hz with strain ranging from 0.01 to 20. A Peltier plate was used to maintain a temperature of 25°C during rheological measurements.

2.3. Morphological Observation

The self-assembled structures of the compounds were observed by a TEM (JEM-140, JEOL Corporation, Tokyo, Japan). An organogelator was dissolved in isododecane, and the sample was attached to a support film grid and dried for 2 h. The sample was then stained by osmium tetroxide 2% aqueous solution for 4 h. The accelerating voltage of the TEM was 100 kV.

3. Results and Discussion

3.1. Effects of Chemical Side Chains of Compounds (1 - 7) on the Solubility and Rheology to Isododecane

Table 2 shows the solubility evaluated by absorbance measurement of 0.5 wt% isododecane with synthesized compounds (1 - 7) at 25°C. Since compounds **6** and **7** (dark grey cells) showed poor solubility and had precipitation, we judged the compounds to be ineffective. Compound **5**, having high solubility (white cell), showed an absorbance of 96.1%; however, the other samples had a cloudy appearance (grey cell). No clear relationship between the solubility of compounds and the length of the alkyl side chain (R') is found from the results in **Table 2**.

The equilibrium flow curves (shear viscosity η versus shear rate $\dot{\gamma}$) for isododecane with the addition of 0.5 wt% compounds **1 - 5** are displayed in **Figure 2**. Pure isododecane, which had a viscosity of 1.2 mPa·s, showed a Newtonian property, while all the samples with compounds presented typical shear thinning properties, which

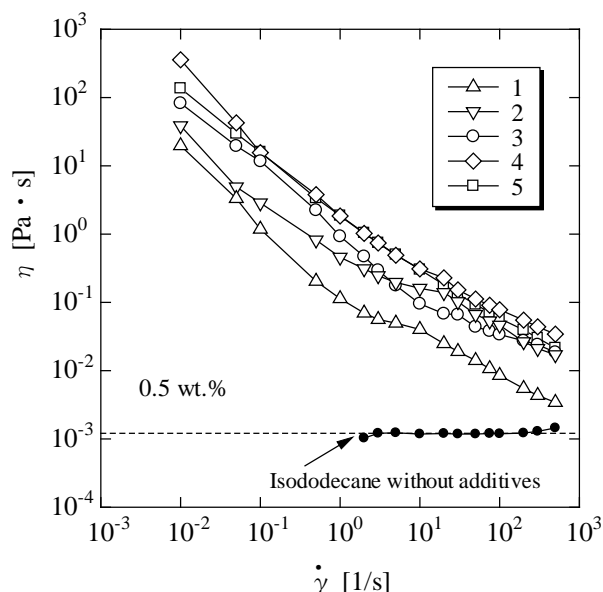


Figure 2. Equilibrium flow curves of 0.5 wt% synthesized compounds in isododecane.

Table 2. Solubility of compounds (1 - 7) to isododecane.

	Compound No.						
	1	2	3	4	5	6	7
Absorbance (%)	5.7	35.8	69.4	24.1	96.1		

may have been caused by the interaction of compound molecules. Viscosities at $\dot{\gamma} = 1 \text{ s}^{-1}$ increased 95, 382, 774, 1536, and 1555 times with the addition of compounds **1** - **5**, respectively, with respect to the original solvent (relative viscosity). These values were in the order of the length of the side chains; however, the trend was established only at particular shear rates.

The dynamic viscoelastic properties of compounds **1** - **5** in isododecane are displayed in **Figure 3**. In the case of compound **1**, G'' is higher than G' at a lower frequency of oscillation, in which the solution showed a viscous rather than elastic property. Since the relation of magnitude reversed at a high frequency of $\omega = 18 \text{ rad/s}$, the relaxation time can be calculated as 0.05 s (reciprocal of 18 rad/s). The absolute values of G' and G'' for compounds **2** and **3** are higher than that for compound **1**. This finding coincides with the increase in relative viscosities shown in **Figure 2**. Because the relaxation times of compounds **2** and **3** are almost the same as that of compound **1**, their self-assembly structures may not be very different in terms of the size and their relations. In the case of compound **4**, G' is always higher than G'' and the relaxation time disappears, indicating the solution has a significant elastic property. In fact, compound **4** loses its fluidity and forms a hard gel when we increase the concentration up to 1.0 wt%. Compound **5** also has no relaxation time with lower absolute values of G' and G'' . The solution is a soft gel with some fluidity.

3.2. Effect of Skelton of Amid Compound

We reported [15] that PMDA having two oleyl and two 2-ethylhexyl (**Figure 4**) showed significant viscosity-increasing effects in several hydrophobic fluids. In this study, the relative viscosity of 0.5 wt% PMDA at $\dot{\gamma} = 1 \text{ s}^{-1}$ was measured as 2148 for isododecane. The viscoelastic properties of 0.5 wt% compound **5** and PMDA in isododecane are displayed in **Figure 5**. We found that PMDA solution has a long relaxation time of several seconds.

Figure 6 shows the strain dependences of G' for compound **5** and PMDA. In spite of the higher G' value of compound **5** at the lower strain region, G' suddenly decreased at the lower strain compared with PMDA. From this result, we found that the self-assembly structure of compound **5** is weaker than that of PMDA.

The morphology of compound **5** was studied by TEM. **Figure 7(a)** shows compound **5** in isododecane, in

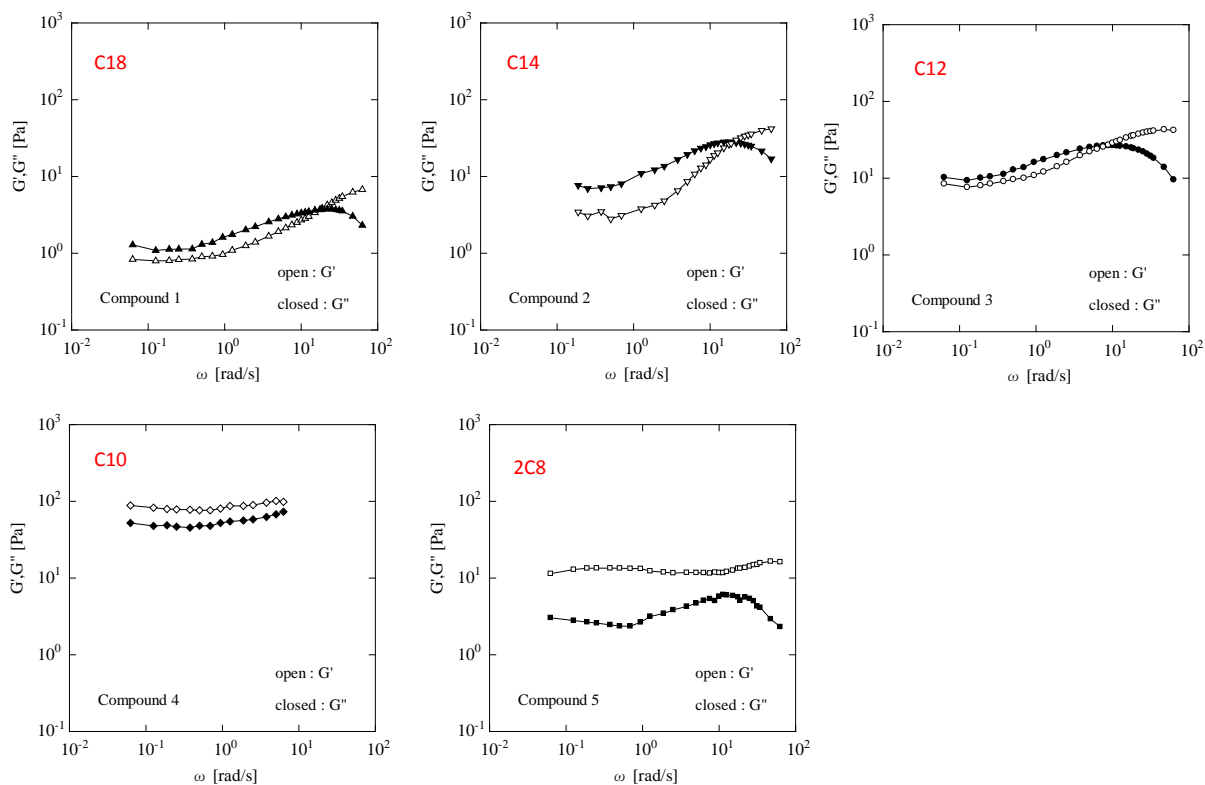
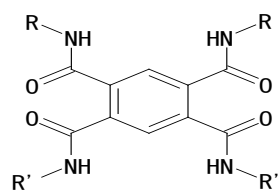


Figure 3. Viscoelastic properties of 0.5 wt% synthesized compounds in isododecane.



R: Olyle R': 2-ethylhexyl

Figure 4. Chemical structures of N,N',N'',N'''-1,2,4,5-tetraalkyl/alkenyl promellitimide (PMDA).

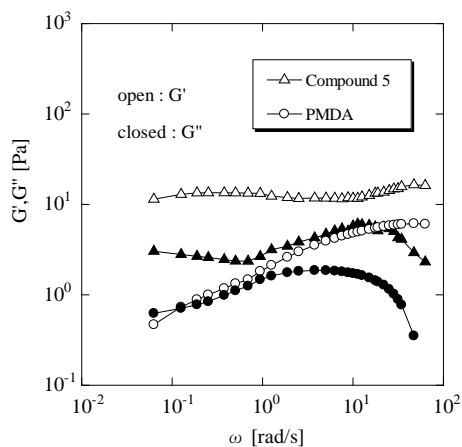


Figure 5. Viscoelastic properties of 0.5 wt% compound 5 and PMDA in isododecane.

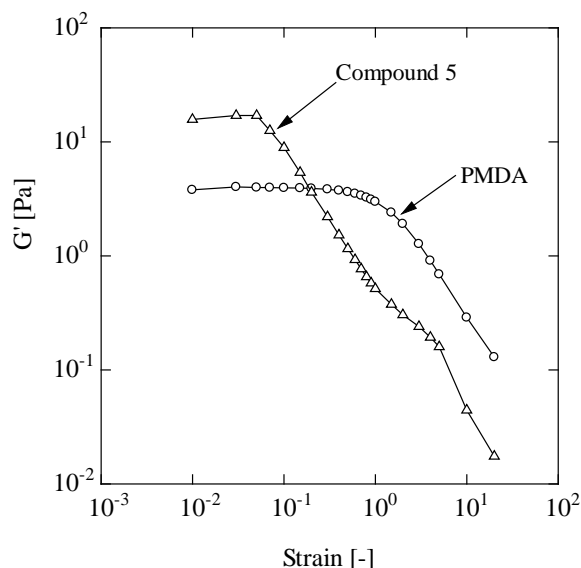


Figure 6. The strain dependences of G' for compound **5** and PMDA.

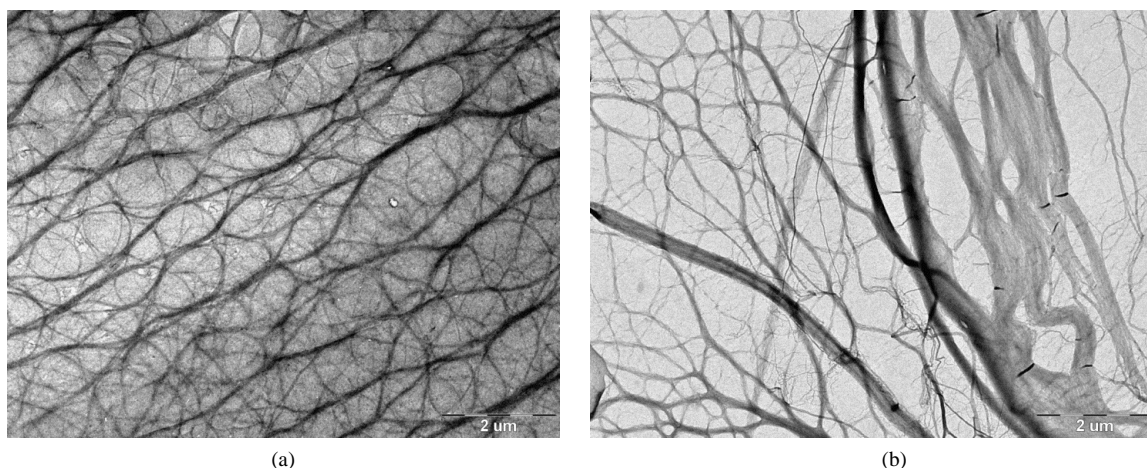


Figure 7. TEM images of gel network formed by (a) compound **5** and (b) PMDA in isododecane.

which fibrous molecules with diameters of ca. 5 - 10 nm can be observed. The presence of such minute self-assembled structures might have contributed to the increasing viscosity in isododecane. The morphology of PMDA with the same alkyl side chains is shown in **Figure 7(b)** for comparison. We found that compound **5** builds a more minute network than PMDA.

The strength of the hydrogen bonding interaction was estimated by calculating the binding energy between a molecule of compound **5** and one of PMDA. The calculation was conducted using SCIGRESS Ver. 2.3 (Fujitsu Co., Tokyo, Japan) with PM5. **Figure 8** shows the obtained coordinate structures consisting of two molecules, in which hydrogen atoms of an amide group are coordinated to the oxygen atom of an amide in another molecule. Such “one on top of another” structures stack repeatedly; consequently a wormlike structure is formed with self-assembly. Although the distance between hydrogen bonds is almost the same for compound **5** and PMDA, the TEM images of the wormlike structures shown in **Figure 7** were clearly different from each other. The slight difference in the binding energy between two molecules may be related to the morphological differences; however, further research is needed to clarify the formation of the network structure.

4. Conclusion

Butane 1,2,3,4-tetracarboxamides were newly synthesized by varying their chemical side chains. The solubili-

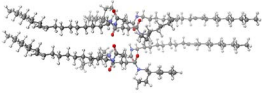
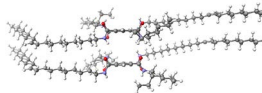
Coordinate structure consisting of two molecules	Binding energy between two molecules (kcal / mol)	Distance between hydrogen bonds (Å)
 Compound 5	-11.3	2.738
		2.742
		2.564
		2.562
 PMDA	-13.1	2.587
		2.677
		2.663
		2.555

Figure 8. Calculation of coordinated structures, binding energy between two molecules, and distance between of hydrogen bonds for compound 5 and PMDA.

ties and rheological properties of compounds **1 - 7** were evaluated to obtain information valuable for the synthesis of effective synthesis of organogelators in isododecane. Self-assembled structures of the compounds' molecules might be related to the rheological properties of compounds in isododecane. The hydrogen bonding of the amide group may become the core of the self-assembled structure, while the alkyl side chains might contribute the affinity of the core molecule to the solvent, which can be controlled by the solubility and crystallinity of compounds. The degree of the expanse might be related to the entanglement of each self-assembled structure. Also, the rheological properties of the compounds are related not only to the degree of entanglement but also to the rigidity of the structures, which can in some cases produce viscoelastic properties.

References

- [1] Steed, J.W. (2011) Supramolecular Gel Chemistry: Developments over the Last Decade. *Chemical Communications*, **47**, 1379-1383. <http://dx.doi.org/10.1039/c0cc03293j>
- [2] Lehn, J.-M. (2002) Supramolecular Polymer Chemistry—Scope and Perspectives. *Polymer International*, **51**, 825-839. <http://dx.doi.org/10.1002/pi.852>
- [3] Bosman, A.W., Brunsveld, L., Folmer, B.J.B., Sijbesma, R.P. and Meijer, E.W. (2003) Supramolecular Polymers: From Scientific Curiosity to Technological Reality. *Macromolecular Symposia*, **201**, 143-154. <http://dx.doi.org/10.1002/masy.200351117>
- [4] Brunsveld, L., Folmer, B.J.B., Meijer, E.W. and Sijbesma, R.P. (2001) Supramolecular Polymers. *Chemical Reviews*, **101**, 4071-4098. <http://dx.doi.org/10.1021/cr990125q>
- [5] Ciferri, A. (2002) Supramolecular Polymerizations. *Macromolecular Rapid Communications*, **23**, 511-529. [http://dx.doi.org/10.1002/1521-3927\(20020601\)23:9<511::AID-MARC511>3.0.CO;2-F](http://dx.doi.org/10.1002/1521-3927(20020601)23:9<511::AID-MARC511>3.0.CO;2-F)
- [6] Velten, U. and Rehahn, M. (1996) First Synthesis of Soluble, Well Defined Coordination Polymers from Kinetically Unstable Copper(I) Complexes. *Chemical Communications*, **1996**, 2639-2640. <http://dx.doi.org/10.1039/cc9960002639>
- [7] Hofmeier, H., Hoogenboom, R., Wouters, M.E.L. and Schubert, U.S. (2005) High Molecular Weight Supramolecular Polymers Containing Both Terpyridine Metal Complexes and Ureidopyrimidinone Quadruple Hydrogen-Bonding Units in the Main Chain. *Journal of the American Chemical Society*, **127**, 2913-2921. <http://dx.doi.org/10.1021/ja042919e>
- [8] Hilger, C. and Stadler, R. (1990) New Multiphase Architecture from Statistical Copolymers by Cooperative Hydrogen Bond Formation. *Macromolecules*, **23**, 2095-2097. <http://dx.doi.org/10.1021/ma00209a037>
- [9] de Greef, T.F.A., Smulders, M.M.J., Wolfs, M., Schenning, A.P.H.J., Sijbesma, R.P. and Meijer, E.W. (2009) Supramolecular Polymerization. *Chemical Reviews*, **109**, 5687-5754. <http://dx.doi.org/10.1021/cr900181u>
- [10] Terech, P. and Weiss, R.G. (1997) Low Molecular Mass Gelators of Organic Liquids and the Properties of Their Gels.

Chemical Reviews, **97**, 3133. <http://dx.doi.org/10.1021/cr9700282>

- [11] Jang, W.-D. and Aida, T. (2004) Supramolecular Nanofiber Formation of Macrocyclic Dendrimer. *Macromolecules*, **37**, 7325-7330. <http://dx.doi.org/10.1021/ma0492364>
- [12] Hanabusa, K. and Suzuki M. (2009) Gelators Bringing about Gelation and Thickeners Raising Viscosity. *SEN'I GAKKAISHI*, **65**, 159-165. http://dx.doi.org/10.2115/fiber.65.P_159
- [13] Hanabusa, K., Koto, C., Kimura, M., Shirai, H. and Kakehi, A. (1997) Remarkable Viscoelasticity of Organic Solvents Containing Trialkyl-1,3,5-benzenetricarboxamides and Their Intermolecular Hydrogen Bonding. *Chemistry Letters*, **26**, 429-430. <http://dx.doi.org/10.1246/cl.1997.429>
- [14] Sakanishi, Y., Narusaka, Y., Itoh, M. and Saeki, T. (2014) Rheology Control of Isododecane with Newly Synthesized Organogelators; 3,3',4,4'-Benzophenone Tetracarboxamide. *Nihon Reoroji Gakkaishi*, **42**, 185-190. <http://dx.doi.org/10.1678/rheology.42.185>
- [15] Sakanishi, Y., Narusaka, Y., Itoh, M., Arita, T. and Saeki, T. (2014) Development of New Organogelators: N,N',N'', N'''-1,2,4,5-Tetra Aalkyl/Alkenyl Pyromellitimides through the Linkage of Their Molecular Design and Rheological Evaluations. *Nihon Reoroji Gakkaishi*, in printing.
- [16] Ferry, J.D. (1989) *Viscoelastic Properties of Polymers*. 3rd Edition, Wiley, New York, 11-12.