学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士(ソフトマター科学)　氏　名　竪山　瑛人

学 位 論 文 題 名

Development of Functional Gels Based on Alkyl–π Molecular Liquids
(アルキルーπ分子液体を媒体とする機能性ゲルの創成)

The development of optoelectronically-active soft matter is drawing attention to the application of soft electronics and soft robotics. Among advanced soft matters, alkyl–π liquids, which are designed as bulky yet flexible branched-alkyl chains attached to a π-conjugated moiety, are attracting particular attention due to their unique characteristics such as fluidity, free deformability, low environmental impact owing to solvent-free handling, and solvent-like functions of dissolving other molecules or nanomaterials. Fluidity of alkyl–π liquids with consistent optoelectronic properties has the advantage of shape adaptability when applied to soft electronic devices; however, there are concerns about liquid leakage and bleeding from devices. One possible solution to overcome this issue is to tune the elastic modulus (G') while preserving the softness and optoelectronic functionality of the alkyl–π liquids. Since G' of most human body organs is between 10^1 to 10^5 Pa, the applications of the alkyl–π liquids in medical and nursing care will be greatly expanded if G' of the alkyl–π liquids can be tuned in this region. So far, the complex viscosity ($|\eta^*|$) and G' of the alkyl–π liquids have been controlled by altering the substitution position and the length of the branched-alkyl chains. The strategy of increasing G' has also been demonstrated in the case of alkyl–π conjugated polymer fluids, where G' can be controlled by more than five orders of magnitude depending on the branched alkyl chain length. However, since arranging the chemical structure for every alkyl–π conjugated polymer fluid is a complicated and time-consuming process, a facile method to control G' over a broader range is required to expand the usefulness of the alkyl–π liquids. The most helpful technique for dramatically and usefully increasing G' of liquids is gelation. Therefore, the study employed low-molecular-weight gelators to develop the gels based on the alkyl–π liquids, i.e., alkyl–π gels, to increase G'.

In Chapter 2, gelations of various alkyl–π liquids, including alkyl–naphthalene, –carbazole, –dicyanostyrylbenzene, and –pyrene liquids by low-molecular-weight gelators were investigated. These alkyl–π liquids show a variety of fluorescent colors (*e.g.*, blue, green, and light blue) and $|\eta^*|$ between 0.046 Pa s and 17 Pa s depending on the structure of the π-conjugated unit and length of the branched alkyl chains. *N*,*N*'-((1*R*,2*R*)-cyclohexane-1,2-diyl)didodecanamide (***RR*-GA1**), which has two amide units and is known for effectively gelating low-polarity organic solvents and liquid crystals by forming fibrous self-assembled structures, was employed for forming gels based on these alkyl–π liquids. Despite the wide variety of optical properties and viscosity, every alkyl–π liquid investigated in this study could be gelated by 1 wt% ***RR*-GA1**, resulting in significant increase of G' from 10^{-4}–10^{-2} Pa to 10^4–10^5 Pa while retaining their optical properties, which were evaluated by absorption and fluorescence spectra, fluorescence lifetime and quantum yield. Among these alkyl–π liquids, the fundamental properties of the gels based on alkyl–naphthalene liquids were further investigated by comparing them to the other low-molecular-weight gelator, 1-(2-benzylphenyl)-3-dodecyl urea (**GA2**), which has been reported to gelate a wide range of liquids, from low-polarity organic solvents to ionic liquids. Translational motion evaluated by ^{1}H NMR stimulated echo method and transparency of the gels were different depending on the gelator because the thickness of the fibrous structure

was different between ***RR*-GA1** and **GA2**. However, in any gels, translational motion retained more than 80% of the neat liquid state, which is advantageous for exhibiting functionalities based on the fluidity peculiar to alkyl–π liquids in the gel state. As for healthcare device applications, stretchable mechanoelectric generator-electret devices (MEGs) were focused on. Alkyl–π liquids have an electroactive π-moiety wrapped with insulating alkyl chains, making them suitable for storing electrostatic charges inside the liquid and functioning as liquid electrets. This study revealed that the gelation with 1 wt% ***RR*-GA1** enhanced the charge density of the electret based on alkyl–pyrene liquid by 24% and open-circuit voltage of MEGs when a vibration of 16.7 Hz was applied to the device by 83 ± 4% compared to the case of neat liquid electret. Importantly, no liquid leakage from the gel MEG devices was observed. Thus, it was confirmed that gelation of alkyl–π liquids is a superior method for tuning G' while maintaining deformability suitable for soft electronics applications.

Focusing on the chiral centers both alkyl-π liquids and ***RR*-GA1** possess, the influence of chirality on the physical properties of the alkyl–π liquids was investigated in Chapter 3. So far, the effect of chirality of the branched alkyl chains in alkyl–π liquids on physical properties has not been investigated. Hence, the fundamental characteristics of chiral alkyl–π liquid compounds were investigated at first. In this study, alkylated carbazole derivatives possessing a racemic (***rac*-C_2C_6CZL**) or an (*R*)-isomeric (***R*-C_2C_6CZL**) 2-ethylhexyl chain were utilized. Both compounds were obtained as solvent-free blue-fluorescent liquids and maintained a liquid state over 6 months at 21 ± 2 °C. The thermal properties of these liquids were investigated by differential scanning calorimetry (DSC). When heated at 0.2 °C/min from a glass state (−80 °C), ***R*-C_2C_6CZL** showed peaks of melting at higher than room temperature after cold crystallization, whereas ***rac*-C_2C_6CZL** did not show an event of cold crystallization. Therefore, the as-obtained ***R*-C_2C_6CZL** was a supercooled liquid at room temperature; in contrast, ***rac*-C_2C_6CZL** was a practically stable liquid. Importantly, because of polymorphism, ***R*-C_2C_6CZL** showed different melting points (m. p.) at 25 °C or 35 °C depending on the thermal treatment. To form gels based on these alkyl–carbazole liquids, in addition to ***RR*-GA1**, (*S*,*S*)-isomer of ***RR*-GA1** (***SS*-GA1**) was employed. Critical gel concentration and G' of the gels measured for the same gelator concentration differed depending on the chirality, suggesting that the formations of the fibrous structure of ***RR*-GA1** and ***SS*-GA1** were influenced by chirality. Notably, the gels based on ***R*-C_2C_6CZL** were stable at room temperature over 6 months even though they are based on the supercooled liquid. Thus, unprecedented long-time stable supercooled gels were developed in this study. When DSC and temperature-dependent X-ray diffraction confirmed phase transition behaviors of the gels, 1 wt% ***R*-C_2C_6CZL/*SS*-GA1** showed the formation of only one crystal structure whose m. p. was 25 °C when heated up at 0.5 °C/min from −35 °C; in contrast, 1 wt% ***R*-C_2C_6CZL/*RR*-GA1** showed solid-solid phase transition between different crystal structures at around 25 °C under the same temperature treatment. These results indicate that the phase transition behavior of supercooled chiral alkyl–carbazole liquid could be controlled by the chirality of the gelators. Based on these findings, further study for controlling the phase transition behavior of supercooled liquids is expected to lead to the development of novel stimuli-responsive materials.

In conclusion, gelation of alkyl–π liquids by low-molecular-weight gelators is a superior method to tune the properties including viscoelasticity, electrostatic charge retention ability, and phase transition behavior while retaining fluidity and intrinsic optoelectronic functionalities. Since conventional π-gels have π-moieties in gelator molecules and employ volatile solvents, their content of π-moieties is only a few wt%, and they quickly dry in the air. In contrast, the alkyl–π gels have a large content of π-moieties up to 59 wt% and are low volatile, which enables them to be handled stably in the air for a long time. To further expand the types of alkyl–π gels and realize more advanced functions, the promising direction of future research is to introduce stimuli-responsive units into gelator molecules. Further study of alkyl–π FMGs will enable the development of novel functional gels that can be applied to various fields such as healthcare, sensing, and soft robotics.