

Room Temperature Liquid Fullerenes: An Uncommon Morphology of C₆₀ Derivatives

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Morphology of nanosize carbon-rich compounds has recently received considerable attention because bulk properties of such carbon materials can be enhanced by fine-tuning of the intermolecular interactions.¹ For example, a highly electroconductive polymer/carbon nanotube composite material possessing substantial dynamic hardness was realized by efficiently dispersing single-walled carbon nanotube bundles within an ionic liquid.² Another approach for control of the morphology of carbon materials is to modify the chemical structure using synthetic methods. One of the most frequently investigated examples is C₆₀. Many functional groups have been introduced, often regio- or stereoselectively, for tuning of the physical properties of C₆₀ and for construction of supramolecular architectures.³ Recently, we reported supramolecular fullerene nanoarchitectures utilizing the two different intermolecular forces introduced by C₆₀ (sp² carbons) and alkyl chains (sp³ carbons).⁴ In the course of this study, we discovered serendipitously that fulleropyrrolidines substituted with a 2,4,6-tris(alkoxy)phenyl group exhibit a fluid phase at room temperature. There have been some reports of room temperature fluid C₆₀ derivatives,⁵ but their properties have remained relatively unexplored.⁶ Here we present a new design concept for liquid fullerenes and report for the first time a detailed study of the rheological, electrochemical, and charge-carrier transport properties of these liquid fullerenes. They are single component nanocarbon materials with high fluidity, which showed the potential use in materials applications.

Fullerenes **1–4** were synthesized by refluxing the 2,4,6-tris(alkoxy)benzaldehyde with *N*-methylglycine and C₆₀ in dry toluene. Fullerene **1** is a dark brown solid with a melting point of 147–148 °C, while the other fullerenes **2–4** are dark brown oils at room temperature (residual solvent was determined to be <0.05 wt %). It should be noted that the melting points dramatically decrease from **1** to **2**, a fact that is correlated with the length of alkyl chains surrounding C₆₀. On the basis of molecular modeling, the length of an octyl chain in an *all-trans* conformation is estimated to be 9.0 Å, whereas that of a dodecyl chain is 14.0 Å. Judging from the diameter of C₆₀ (7.1 Å), three dodecyl chains are expected to serve as an effective steric stabilizer preventing C₆₀ aggregation, resulting in a fluid phase. Generally, a higher plasticity of stabilizers promotes the isolation of a fullerene core so that a greater alkyl chain length results in a more fluid fullerene (*vide infra*).

Remarkably, we found that when *n*-hexane or *n*-heptane solutions of **4** are slowly evaporated at room temperature a brown solid is obtained (Figure 1b). Evaporation of solutions of **4** in other solvents, such as CHCl₃ and CH₂Cl₂, does not produce a solid but a liquid. Careful integration of the ¹H NMR spectrum of **4** together with its thermogravimetric analysis demonstrated an absence of residual solvent in these solid forms. The X-ray diffraction (XRD) analysis

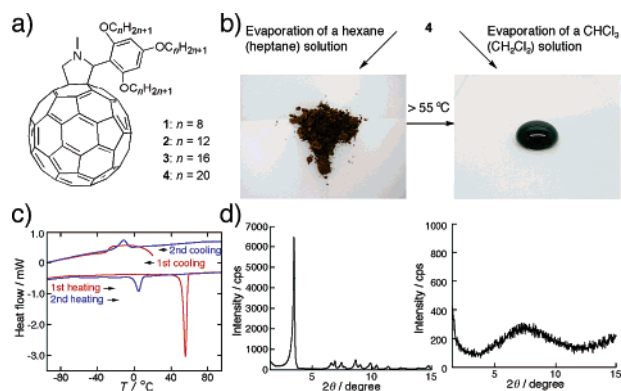


Figure 1. (a) Structure of C₆₀ derivatives (**1–4**). (b) Photographs of **4** after evaporation from different solvents, (c) the DSC thermograms of a sample of **4** prepared by slow evaporation of an *n*-hexane solution, and (d) XRD diffraction patterns of the solid (left) and liquid (right) forms of **4**.

at 20 °C indicated a more extended conformation of the alkyl chains in the solid form. The liquid form exhibits a very broad peak at $2\theta \approx 7.4^\circ$ ($d = 1.2$ nm) like **2** and **3**, whereas the solid form shows well-defined diffraction patterns with the most intense diffraction peak at $2\theta = 3.5^\circ$ ($d = 2.5$ nm) (Figure 1d). The d spacing is similar to an eicosyl chain length in an *all-trans* conformation. Volatile alkanes are thought to assist the orientation of eicosyl chains of **4** and, consequently, furnish solid C₆₀ assemblies in various packing lattices.⁷ Comparison of differential scanning calorimetry (DSC) data of the solid and liquid samples gives more meaningful results. The first cooling scan of the solid sample **4** does not contain any distinct transitions below room temperature, but the subsequent heating scan exhibits a very sharp endothermic peak at 55 °C, which does not appear in the DSC trace of the liquid form (Figure 1c). The enthalpy and entropy at this transition temperature are $\Delta H = 92.1$ kJ mol⁻¹ and $\Delta S = 166.8$ J mol⁻¹ K⁻¹, respectively. The entropy value is in fairly good agreement with the total entropy of phase transition for the alkyl chains ($\Delta S = 115.8$ J mol⁻¹ K⁻¹ is estimated for the three eicosyl chains since $\Delta S = 1.93$ J mol⁻¹ K⁻¹ per methylene unit)⁸ and the C₆₀ part ($\Delta S = 30$ – 40 J mol⁻¹ K⁻¹).⁹ The temperature of this transition has been ascribed to the melting point. In the second cycle, the corresponding exothermic peak does not appear upon cooling and the phase behavior is identical with the liquid form (Figure 1c). The appearance of the sample during the second cycle does not change even below the glass transition point. These results reveal that the liquid form is the more stable state and that the solidification induced by precipitation from volatile alkanes results in a metastable state. Note that this metastable state is only observed for **4**, which contains the longest alkyl chains in this study.

The rheological behavior of the fluid fullerenes **2–4** was investigated at 25 °C. For all the fullerenes studied and over the measured frequency range, the loss modulus G'' is higher than the

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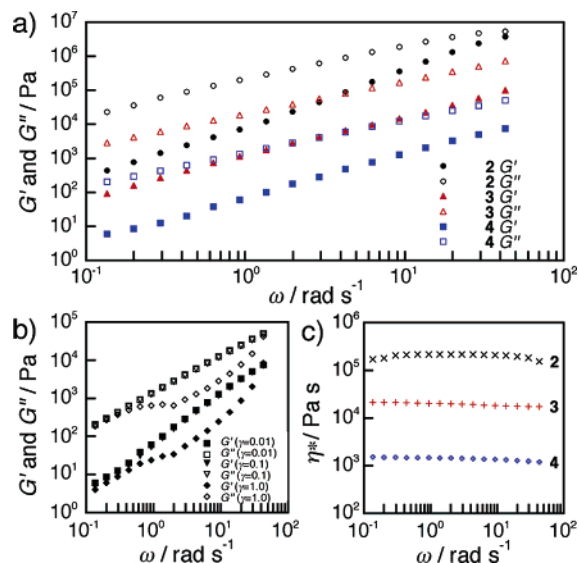


Figure 2. Rheological behavior of liquid fullerenes at 25 °C. Angular frequency dependence of (a) storage and loss moduli of 2–4 at a γ of 0.01, (b) storage and loss moduli of 4 at γ values of 0.01, 0.1, and 1.0, and (c) the complex viscosity of 2–4 at a γ of 0.01.

storage modulus G' and suggests liquid-like behavior (Figure 2a). The frequency dependence also indicates that a number of components with a long relaxation time exist for each sample, which may reflect cluster formation and complex dynamics. When the strain amplitude (γ) is increased from 0.01 to 1.0, the G' curve of 2 deviates upward in the low-frequency region, implying formation of a structured material (Figure 5 in Supporting Information). In contrast, the curve of 4 deviates downward upon an increase in γ , indicating that the initially existing structure is broken (Figure 2b). The emergent structure in 2 might be derived from C_{60} aggregation since the alkyl chains are barely of sufficient length to isolate the C_{60} core, but the initial structure of 4 probably originates in the intermolecular interaction of eicosyl chains. As angular frequency increases, the deviation of G' and G'' curves for 4 is significant at an applied γ value of 1.0. Using the onset frequency of this deviation ($0.628 \text{ rad}\cdot\text{s}^{-1}$) as well as the absolute value of the complex viscosity ($1400 \text{ Pa}\cdot\text{s}$), the effective hydrodynamic radius of the preformed structure of 4 is estimated to be approximately 21 nm. Comparison of the complex viscosity clearly shows that the frictional coefficient between molecules and/or clusters decreases with an increase in the alkyl chain length (Figure 2c). Thus, it is supposed that the friction is mainly derived from the strong interaction between C_{60} moieties.

When considering possible practical applications of liquid fullerenes, it is important to maintain the potentially useful properties of pristine C_{60} .¹⁰ Cyclic voltammograms of 1–4 recorded in CH_2Cl_2 (+0.1 M Bu_4NClO_4) exhibit three well-resolved, reversible reduction steps similar to C_{60} (Figure 6 in Supporting Information). Liquid C_{60} derivatives were also electrochemically active when measured as cast films on a glassy carbon electrode. A cast film of 4 prepared from CH_2Cl_2 solution displayed reversible redox events corresponding to the generation of C_{60} monoanion and dianion at potentials of $E_{\text{red},1} = -0.74 \text{ V}$ and $E_{\text{red},2} = -1.02 \text{ V}$, respectively (Figure 7 in Supporting Information). In contrast, only a single redox wave was observed under the same conditions for a cast film of 4 prepared from an *n*-hexane solution (Figure 7 in Supporting Information). The $E_{\text{red},1}$ potential (-0.73 V) of the metastable solid film is almost the same as that of the liquid form, but the peak current is much lower. The liquid form evidently facilitates the diffusion of supporting electrolytes, the medium (in

this case, water), and the C_{60} -containing molecule itself. This result highlights the advantages of liquid fullerenes. We also found that liquid C_{60} possesses a large carrier mobility. Hole mobility of 4, estimated from transient photocurrent measurements, was $\sim 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 20 °C (Figure 8 in Supporting Information). The value is comparable to those of methanofullerene derivatives in polymer blends as well as smectic liquid crystalline phases of organic conjugated oligomers.¹¹ This result is consistent with the rheological measurements which revealed the preformed structure of 4 in the liquid form.

In summary, the rheology of liquid C_{60} derivatives was investigated for the first time. There is a clear correlation between the viscosity of these liquid fullerenes and the attached alkyl chain length. The liquid fullerenes are electrochemically active and have a relatively large hole mobility. Considering that liquid samples do not suffer from the deleterious influence of domain or grain boundaries, they look promising as novel carbon materials for applications in, for example, carbon electrodes of secondary batteries and electrochemical capacitors. Our findings should be applicable to a variety of higher fullerenes, metallofullerenes, and possibly carbon nanotubes.

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Supporting Information Available: Synthesis of 1–4 and the properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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