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題目(和文)	ESA-CFプロセスのDFT素反応解析に基づく環状高分子側鎖へのペリレン基高密度導入およびトポロジー効果の検討
Title(English)	Topology effects by cyclic polymers having densely-appended perylene groups designed upon the DFT elucidation of elementary reactions in the ESA-CF process
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（工学博士）
学生氏名： Student's Name	木村　彰宏	指導教員（主）： Academic Advisor(main)	手塚　育志
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, a notable self-assembly transformation of spherical micelles into rod-like micelles by the ion-exchange reaction on perylene diimide (PDI) having cyclic ammonium salt groups and a novel topology effect on the electron mobility of cyclic poly(perylene diimide acrylate) (PPerAcr) thin films has been achieved based on the mechanism elucidation of the regioselectivity of azacycloalkane quaternary salts.

In chapter 2, the elucidation on the experimental reaction between cyclic ammonium salt groups and nucleophilic carboxylate groups and the comparison between experimental results and calculated value of thermodynamic energy differences and kinetic energy differences indicated that the regioselectivity in the nucleophilic esterification on cyclic ammonium salt groups was directed by the ring conformation of transition state rather than the ring strain of ground state. The skeletal conformation of the 5-membered cyclic ammonium salt transition state transformed close to the unstrained cyclohexane conformation, which was energetically favorable to cause a selective ring-opening reaction. 6- and 7-membered counterparts had more frustrated conformations and were likely to exhibit favored ring-emitting reactions. For applying this mechanism, dimethyl group was introduced to 6-membered N-phenylpiperidine to construct more frustrated ring-opening transition state. 3,3,-dimethyl-N-phenylpiperidine was newly synthesized and exhibited a selective ring-emitting reaction that constructs simple and robust ester linkages. This selectivity was mainly caused by the 1,3-diaxial interaction between phenyl group and dimethyl group on 6-membered ring, because, similarly, the dimethyl group was introduced into 6-membered thianium group to indicated not selective ring-emitting reactivity from calculation results.

In chapter 3, PDI having 5- and 6-membered cyclic ammonium salt groups (I/TfO^-, II/TfO^-) was novelly synthesized through the triflate esterification reaction and the ammoniation reaction. By applying the ESA-CF process, ionic groups of I/benzoate, I/biphenyldicarboxylate, II/benzoate, II/biphenyldicarboxylate were prepared. The spherical self-assembly or the rod-like self-assembly having different sizes were constructed in aqueous condition based on the hydrophilic interaction and the pi-interaction which was clearly observed by the red shift in UV-vis spectra. TEM images were clearly indicated the formation of self-assembly. DLS results also showed the similar size of self-assembly observed by TEM measurement. And also, the sizes of self-assembly were determined by the combination of the cyclic ammonium cation groups and carboxylate anion groups. The ionic joint direction affected the configuration of the self-assembly. Additionally, the self-assemblies in water were easily transformed by the exchange of their counter anions.

In chapter 4, linear and cyclic poly(t-butyl acrylate) having different molecular weight were synthesized by atom transfer radical polymerization and the continuous ring-closing metathesis reaction. Poly(acrylic acid) and poly(sodium acrylate) were synthesized by the deprotection reaction of t-butyl group and the neutralization reaction. Next ESA-CF technique with cationic PDI, I/TfO^-, generated a densely PDI-appended PPerAcr of which the introduction ratio was 90%, as estimated by UV-vis spectra and elemental analysis. The covalent fixation reaction was conducted by next heating process. In $CHCl_3$ solutions, those synthesized linear and cyclic polymers constructed spherical vesicle like self-assemblies having different sizes along with their chain length and the difference of their topology measured by TEM. Optical microscopic analysis in solution state also indicated the construction of vesicle like structures which had a hollow space in spherical self-assembly. The measurement of viscosity indicates the lower viscidity of cyclic PPerAcr in $CHCl_3$, implying the lower entanglement in the self-assembly of cyclic polymers.

In chapter 5, the topology effect on the electron mobility between linear and cyclic PPerAcr was observed by fabricating electron-only devices supported by the cyclic voltammetry measurements of

PPerAcr to estimate the LUMO levels for the blocking of hole and the electron injection. The measurement was conducted under space charge limited current conditions. The higher carrier mobility of the cyclic polymer thin film was newly observed. Additionally the increment of electron mobility on cyclic polymer was revealed to been derived from their higher film density as estimated by XRR and the combination of microfigure measurement and QCM. This difference of film density was caused by the condensation of polymer at the condition of self-assembly in $CHCl_3$ solution. Additionally, the C/L ratio decrement along with the increase of the chain length indicates that the end group had the greatest role in the electron mobility and film density.

According to these results of chapters 2, 3, 4, and 5, the ESA-CF process was absolutely elucidated by the combination of DFT calculation and experimental results. Additionally, selective ring-emitting reaction was achieved by the introduction of dimethyl group for 6-membered ammonium salt. The PDI groups having cyclic ammonium salts indicated various applicable methodologies demonstrated as a process of transformable self-assembly and side chain introduction. Furthermore, the constructed PPerAcr showed a novel topology effect on electron carrier mobility derived from the film density. Therefore, this methodology promises the construction of various functional cyclic architectures with a distinct topology effect.