

論文の内容の要旨

論文題目 Study of polyrotaxane synthesized via reversible addition-fragmentation chain transfer polymerization

(可逆的付加開裂連鎖移動重合を用いたポリロタキサンの研究)

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1. Introduction

Polyrotaxane (PR) is a supramolecule composed of linear polymer chains threaded with ring molecules, end-capped by bulky groups on the chain ends. Ring molecules can slide along the chain since there is no fixed bonding between rings and linear chains. In 2001, Ito et. al prepared a slide-ring gel (SRG) from PR based on α CD by crosslinking ring molecules on PR to obtain movable crosslinking points in the gel.³ SRG is known as a resilience material compared to fixed crosslinked gel (FCG) because of movable crosslinking points known as pulley effect (Fig.1).

Conventional method for PR preparation is shown in Fig.2. First, PPR was formed from ring molecules spontaneously complexed with linear polymer chains during continuous stirring. Then PR was prepared by modification of linear chain ends into bulky group. This method has widely developed in many applications. Recently, an alternative way of PR synthesis was reported as a copolymerization of monomer/CDs inclusion complexes and a stopper monomer with a bulky side chain.^{5,6} In this study, PR synthesized from inclusion complexes via reversible addition-fragmentation chain transfer (RAFT) polymerization was investigated. First, statistical copolymers based on monomer/CDs inclusion complexes were synthesized and availability of various stopper monomers were investigated. Then triblock copolymer of PR was synthesized utilizing RAFT polymerization in two steps to obtain a PR with a well-defined structure. Various conditions of CD and MMA were used for synthesis of PR to investigate the relationship with the PR coverage. Finally, SRG was prepared from PR and compared with a conventional fixed crosslinked gel.

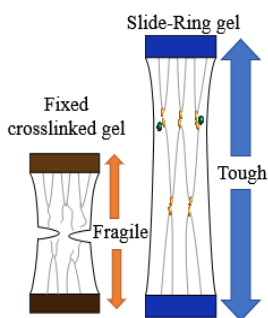


Fig.1 Illustration of FCG and SRG.

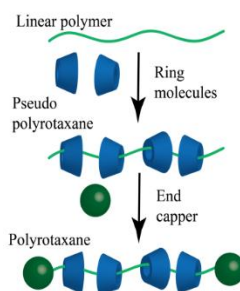


Fig.2 Conventional preparation method of PR

2. Polyrotaxane as statistical copolymer via RAFT

To investigate a proper stopper monomer for PR preparation, N-(3-(dimethylamino) propyl) methacrylamide (DMAPMA), poly (ethylene glycol) methyl ether methacrylate (PEGMA, MW=300) and 2-hydroxyethyl methacrylate (HEMA) were applied as hydrophilic monomers with a bulky side chain for the preparation of PR. Statistical PR was synthesized via conventional copolymerization with stopper monomer and inclusion complexes of methyl methacrylate (MMA) and gamma CD (γ CD). After purification by dialysis and centrifugal precipitation, white powder was obtained by lyophilization.

From Gel permeation chromatography (GPC) result, free γ CD wt% was calculated from the peak in small MW region using the calibration curve of γ CDs. The result of nuclear magnetic resonance (NMR) and diffusion ordered spectroscopy (DOSY) spectrum is shown in Fig.3. Characteristic peaks of γ CD at 4.2ppm, 4.8ppm were found in the NMR spectrum. Integral areas for A(0.5-1.2ppm), B(4.2ppm), and C(2.9-3.1ppm) were used to calculate to get total wt% of γ CD in the polymer and threaded γ CD wt% was obtained by subtracting free γ CD wt% from total wt% of γ CDs. The coverage ratio was calculated as molar ratio of γ CDs to MMA multiply by 2.5 considered that 1 unit rCD covers 2.5 units of MMA. In DOSY analysis, diffusion coefficients of γ CD peaks were calculated as around $8 \times 10^{-10} \text{ m}^2/\text{s}$ as higher mobility for free γ CDs and $5 \times 10^{-11} \text{ m}^2/\text{s}$ as lower mobility for γ CDs where considered to be threaded on the polymer main chain since the value was aligned with diffusion coefficients of polymer main around area A.

Results of PR coverage for various stoppers are shown as Table1. HEMA was not bulky enough and many γ CDs were dethreaded through purification for resulting PR with coverage ratio less than 2%. The coverage ratio of PR synthesized from PEGMA was 58.3% as the highest result suggested that bulkier side chains block CDs more efficiently. To testify the affinity of stopper and γ CD, stopper was mixed with γ CD without monomer for 30min. γ CD+PEGMA solution became turbid because of the inclusion complexes formation that γ CD threaded on the PEG side chain of PEGMA⁹. On the other hand, γ CD-DMAPMA solution was clear, suggested that no complex formed between DMAPMA and γ CD. To prevent bias of coverage calculation, DMAPMA was selected as the stopper for the following synthesis procedure.

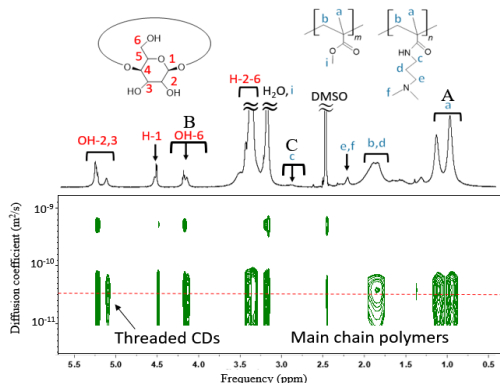


Fig.3. NMR and DOSY spectrum of PR made by statistical copolymerization of MMA, DMAPMA with BDATC. Measured in 25°C in d_6 -DMSO.

Stopper	Coverage
PEGMA	58.3%
DMAPMA	17.7%
HEMA	<2%

Table.1 Coverage of PR synthesized with various stoppers. [Stopper]=100mM, [MMA]=300mM, [BDATC]=10mM, [γ CD] =300mM, [VA44] =5mM.

3. Polyrotaxane as a triblock copolymer via RAFT polymerization

There are two steps for synthesis of polyrotaxane as a triblock copolymer. First, DMAPMA was polymerized with CTA as a polystopper using 4,4'-azobis (4-cyanopentanoic acid) (ACVA) as an initiator. In the second step, polystopper and γ CD were dissolved in 8M urea solution, followed by MMA addition, and stirred for 30 min. Polymerization was initiated by VA44 under 50°C and reacted for 24hrs. Products were purified by centrifugation to remove free γ CDs. White powder was obtained after lyophilization.

First order kinetic plot of polystopper synthesis is shown in Fig.4. The linear relationship of conversion and molecule weight suggested that polystopper synthesis was mediated by CTA. Polydispersity index (PDI) of the polystopper slightly increased to 1.4 due to possible decomposition of thiocarbonate in the synthesis of polyacrylamide. In the result of GPC analysis, Mw grow from 17k of polystopper to 505k of PR was observed and a unimodal peak was exhibited in the GPC curve. This suggests PR were synthesized with mediation of polystopper to be a block copolymer. To evaluate the RAFT behavior, various concentration of polystopper was used to synthesize PRs while [MMA] and [VA44] were fixed as 300mM and 5mM. The apparent chain transfer constant $C_{tr(app)}$ of PMMA radicals to polystopper as marcoCTA was determined by Mayo method. From the plot of reciprocal of degree of polymerization(1/DP) to molar ratio of polystopper to monomer, this method gave $C_{tr(app)}=0.1$ at 50 °C. It is considered as the affinity of chain carriers to mCTA was weakened for the hinderance of γ CDs.

By setting [MMA], [mCTA], and [VA44] to be control variables, the effect of [γ CD] for PR synthesis was investigated. PR with higher coverage was synthesized when higher [γ CD] was applied Fig.5 shows the coverage of resulting PRs from various [MMA] when [γ CD] fixed as 300mM. With more MMA in the reaction system, the coverage became lower while MW increased linearly as a controlled polymerization. CD emulsion was observed in the mixture before reaction in the case of high [MMA]. This suggested that excessed MMA droplets were stabilized by the inclusion complexes. When excessed MMA in CD emulsion was reacted without complexing with γ CD, the coverage became lower. From investigation of main factors for synthesis of PR via RAFT polymerization, PRs with controlled molecular weight from 10k-50k g/mol and coverage from 2%-20% were realized.

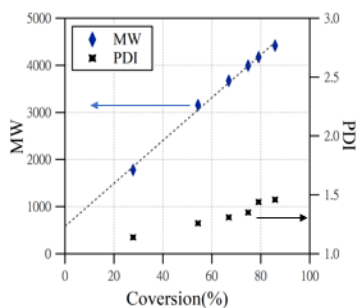


Fig.4 First kinetic plot of polyDMAPMA as a polystopper.

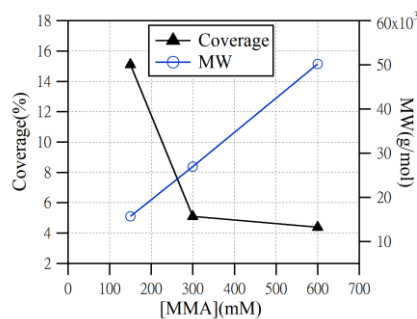


Fig.5 Plot of [MMA] vs coverage and MW of PMMA main chain. [CD] = 300mM, [mCTA] = 10mM, [VA44] = 5mM.

4. Slide-ring gel based on polyrotaxane synthesized via RAFT

For gel preparation, PR was fully dissolved in dry N,N'-dimethylformamide (DMF) as 20wt% solution by 1hr stirring and degassed for 10min. Then 1,1'-carbonyldiimidazole (CDI) was added to the solution as a crosslinker for 2wt%, stirred for another 10min. The solution was poured into a mold for the desired sample shape and heated at 60°C overnight for gelation.

Dynamic mechanical analysis (DMA) result measured in frequency sweep mode at a variety of temperatures is showed in Fig.6. Storage modulus (E') was stable in the temperature range measured. Loss modulus (E'') decreased gradually with increasing temperature as molecular friction was reduced in high temperature so that less energy was dissipated. In this result, gel was confirmed as a chemically crosslinked gel for its sustainable mechanical properties during temperature change.

To investigate the mechanical properties of SRG prepared from PRs, HEMA was used as a fixed hydroxyl group source to compare with movable crosslinking point in SRG. A poly(DMAPMA-*block*-(MMA+HEMA)-*block*-DMAPMA) triblock copolymer was prepared via RAFT as a similar structure with PR as in Fig.7. As the result shown in Figs.8, FCG was broken at 50% strain and not able to recover its original shape while SRG remained contact after 90% strain applied. This suggested that the mechanical properties were improved because of movable crosslinking points in the SRG. For gel prepared from PR with various molecular weight for tensile test, the gel from 60k Mw PR showed better extensibility than the gel from 30k Mw PR. This suggests that sliding distance in the polyrotaxane is needed for the resilience behavior originated from the pulley effect as γ CD sliding along the main chain polymer.

In this study, PR was synthesized via RAFT polymerization as a structure built from inclusion complex of MMA/ γ CD and blocked by PDMAPMA as segments on the chain ends to stop γ CD from dethreading. PRs with molecular weight from 10k-60k g/mol and coverage from 2%-20% were synthesized via RAFT process. The gel prepared from PR showed better toughness than FCG. The tough mechanical properties can be found from the gel with higher molecular because of longer sliding distance within the polyrotaxane. Considered the chemical activity of chain transfer agent and thermal resistivity of PMMA, the thermal and chemical properties of SRG based on PMMA- γ CD are planned to be investigated in the future.

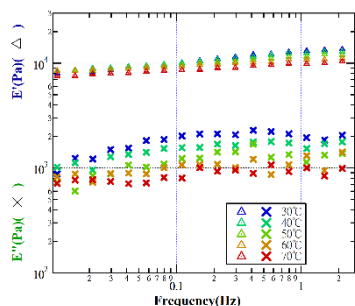


Fig.6 DMA plot of SRG.
Temperature: 30°C-70°C.
Frequency: 0.01Hz-3Hz

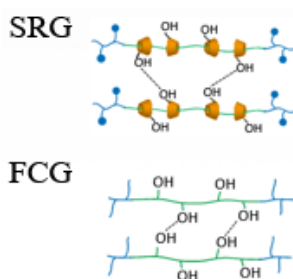


Fig.7 Illustration of
molecular structure of
SRG and FCG.

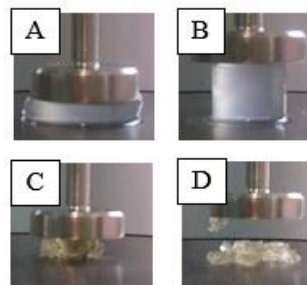


Fig.8 Images of compression tests.
SRG:(A) Under (B) After compression.
FCG:(C) Under (D) After compression.