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学 位 論 文 題 目	Synthesis of New Functional Polymers by Ring-Opening Polymerization of 2-Oxazolines (2-オキサゾリンの開環重合による新しい機能性高分子 の合成)
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## 論 文 内 容 要 旨

Paid attention to the living nature of the polymerization of 2-oxazolines and the unique properties of poly (2-oxazoline), novel functional polymers have been synthesized by ring-opening polymerization of 2-oxazolines.

A nonionic polymer surfactant having a hydrophilic poly (N-acylalkylenimine) segment from a cyclic imino ether monomer has been synthesized, in which a hydrophobic group was introduced by terminating the living end of the propagating polymer ("terminator method"). Monomers used for construction of the hydrophilic segment are 2-methyl-, and 2-ethyl-2-oxazolines and 2-methyl-5, 6-dihydro-4H-1, 3-oxazine. The surfactant properties of the product polymers were evaluated by the surface tension ( $\gamma$ ) of the aqueous polymer solution. Four kinds of terminator were employed: ( i ) with 2-(higher alkyl)- or 2-[3-(perfluorooctyl) propyl]-4, 4-dimethyl-2-oxazoline having reduced polymerizability, the living end of the propagating polymer was terminated, followed by hydrolysis to give the nonionic polymer surfactant having a higher alkyl or 3-(perfluorooctyl)propyl group. ( ii ) 2-n-Octyl- or 2-n-undecyl-5-methyl-2-oxazoline was used as terminator in a similar method. ( iii ) With a primary or secondary (higher alkyl)amine and (perfluoroheptyl)methylamine, the living end of the

polymer was terminated, followed by deionization to produce the polymer surfactant. (iv) A mixture of higher fatty acid and triethylamine was used as a terminator. Using a primary higher alkyl or (perfluoroheptyl) methylamine gave a versatile method for producing effective nonionic polymer surfactants. The lowest  $\gamma$  value via (iii) reached 19.5 dyn/cm for a polymer sample from 2-methyl-2-oxazoline monomer / (perfluoroheptyl) methylamine terminator. Furthermore, solubilization behavior of Oil Yellow OB by the surfactant with a higher fatty acid group in aqueous solution was examined. The solubility ability increased with increasing the carbon number of the alkyl chain.

Block copolymers from tetrahydrofuran (THF) or vinyl ethers with cyclic imino ethers were synthesized by successive cationic copolymerization of each monomer in one-pot procedure. The resulting copolymers had a hydrophobic poly(oxytetramethylene) from THF or poly(vinyl ether) segment and a hydrophilic poly(N-acylalkylenimine) segment from a cyclic imino ether. Vinyl ethers used for construction of a hydrophobic segment are n-butyl, i-octyl, and n-cetyl vinyl ethers. Cyclic imino ether monomers used for construction of the hydrophilic segment are 2-methyl-, and 2-ethyl-2-oxazolines and 2-methyl-5,6-dihydro-4H-1,3-oxazine. These block copolymers exhibit excellent surface activities, and hence, are a group of nonionic polymer surfactants. The surface activities reflected by the surface tension ( $\gamma$ ) in water are very high. The lowest  $\gamma$  value reached 27.6 dyn/cm for the copolymer from n-butyl vinyl ether / 2-methyl-2-oxazoline. The C-N bond between the poly(vinyl ether) segment and poly(N-acylalkylenimine) segment was readily cleaved under acidic conditions to give a mixture of both homopolymers having no surface activities.

Polymerization of 2-alkyl-2-oxazolines was carried out using allyl-type dihalides or xylylene dihalides as a bifunctional initiator in acetonitrile. The allyl-type dihalides used are 1,4-dibromo-2-butene and 3-iodo-2-(iodomethyl)-1-propene and the xylylene dihalides are p-xylylene diiodide, p-, m-, and o-xylylene dibromides. The molecular weight distribution of the resulting polymer evaluated by  $M_w/M_n$  was very narrow. The degree of polymerization of the polymer determined by vapor pressure osmometer (VPO) was very close to the feed ratio of the monomer to initiator. A mixture of corresponding dichlorides and sodium iodide used as an initiator also gave the polymer with narrow molecular weight distribution. Kinetic study of the polymerization of 2-methyl-2-oxazoline was performed using these initiators in  $CD_3CN$  at 35°C. The two initiation rate constants ( $k_{i1}$  and  $k_{i2}$ ) of these initiators determined by  $^1H$  NMR spectroscopy were larger than the corresponding propagation rate constant ( $k_p$ ) except the  $k_{i2}$  value of o-xylylene dibromide. These data indicate that the polymerization using these bifunctional initiators for 2-oxazoline is a "fast initiation - slow propagation system". A multicoupling reaction of poly(2-oxazoline) having two living ends produced by using 1,4-dibromo-2-butene with a tertiary or aromatic diamine gave a poly(2-oxazoline) ionene poly-

mer. Diamines used were N, N, N', N'-tetramethylethylenediamine, 1, 4-diazabicyclo-[2. 2. 2.] octane, and 4, 4'-dipyridyl. The ionene polymer showed typical polyelectrolyte behavior in water.

Poly (2-oxazoline) macromonomer having a polymerizable vinyl ester group or glycol group has been synthesized. The macromonomer having a vinyl ester group was synthesized by polymerizing 2-oxazoline, using vinyl iodoacetate as the initiator. The degree of the macromonomer was close to the feed ratio. The macromonomer showed narrow molecular weight distribution from  $M_w/M_n$  and possessed almost one vinyl ester group per molecule. A mixture of vinyl chloroacetate and sodium iodide can be also used for the synthesis of the macromonomer. From the kinetic study, the initiation rate of vinyl iodoacetate was almost the same as that of propagation. These data indicate the fast initiation and relatively slow propagation system. The block-type amphiphilic poly (2-oxazoline) macromonomer was synthesized by one-pot two-stage copolymerization using a vinyl iodoacetate initiator. The macromonomer possessing a glycol group was synthesized by the termination of the polymer living end with a nucleophile possessing a glycol group. The nucleophiles used were diethanolamine and 2, 2-bis (hydroxymethyl) propionic acid / triethylamine. From  $^1\text{H}$  NMR analysis of the resulting macromonomer, the glycol group was introduced into the end of the polymer quantitatively. Copolyurethane-g-poly (2-oxazoline) was synthesized by copolyaddition reaction of poly ( $\epsilon$ -caprolactone) having a hydroxyl group at both end and 4, 4'-diphenylmethane diisocyanate using the macromonomer as a chain extender.

Polymer particles containing poly(N-acylethylenimine) chain localized on the surface were prepared by soap-free emulsion copolymerization of styrene with a styryl-type poly (N-acylethylenimine) macromonomer. The macromonomer used was highly hydrophilic and soluble in water. The contour of the particles was examined by SEM. The copolymer particles were spherical and monodispersed. The average diameter of the particles was in the range of sub-micron size and smaller than that of polystyrene particles prepared in a similar way without the macromonomer. The surface composition of the particle was analyzed by ESCA. It has been found that poly (N-acylethylenimine) chains are present locally on the particle surface.

Dispersion polymerization of methyl methacrylate (MMA) in an aqueous methanol solution was carried out using poly (2-ethyl-2-oxazoline) (PEtOZO) as a steric stabilizer. The dispersion polymerization in the aqueous methanol solution (methanol:water = 70:30 weight %) gave particles with narrow size distribution in the range of micron size. The diameter of the particles decreased as the molecular weight of PEtOZO increased. Effects of other polymerization parameters such as monomer and initiator concentrations, solvent composition, and addition of methyl 2-methylpropionate on the size and size distribution of the particles have been examined.

## 審査結果の要旨

高分子の新材料を創製するには、それらをつくる反応をよく理解し、特徴を活かし、構造の制御された高分子を設計、合成することが不可欠である。著者は環状1,3-オキサザ化合物の2-オキサゾリン類をモノマーとして用いるカチオン開環重合が容易にリビング的に進行する特徴を利用し、いくつかの新しい機能性高分子を創出している。また、生成高分子の界面活性剤としての特性を活かし、粒径分布の狭いポリマー粒子の新しい合成法を開発している。本論文はこれらの成果をまとめたもので、全編8章よりなる。

第1章は序論である。

第2章では、2-オキサゾリン重合のリビングカチオン生長末端を4種類の求核試薬と反応させ、重合を停止する方法により新規界面活性剤の合成を提案している。ここで合成されたものはポリ(2-オキサゾリン)鎖が親水性基、停止剤が疎水性基として機能する。

第3章では、テトラヒドロフラン (THF) 及びビニルエーテルモノマーのカチオンリビング合成の生長種に第2のモノマーの2-オキサゾリンを加えてその重合をひき起こさせ、AB型ブロック共重合体の非イオン性界面活性剤を得ている。THFについてはABA型ブロック共重合体も得ている。これらは全く新しい型の非イオン性高分子界面活性剤である。

第4章では、2-オキサゾリンのテレケリックポリマーを合成するための新規重合開始剤として二官能性アリル型ハライドが入手し易く、非常に有用であることを示している。この重合系は迅速開始、緩慢生長系であり、分子量分布の狭い高分子を与える。

第5章では、ビニルエステル型重合性基をもつ2-オキサゾリンのマクロモノマーをヨード酢酸ビニルを開始剤とする2-オキサゾリンの開環重合により実現している。また、グリコール反応性基をもつマクロモノマーをも合成している。これらの研究により種々の新しい型のマクロモノマーが実用的に重要な意味をもつことが明らかとなった。

第6章では、ポリ(2-オキサゾリン)鎖が有効な界面活性剤となることを利用して、そのスチリル型マクロモノマーをコモノマー及び乳化剤として機能させるソープフリー乳化共重合によってサブミクロンサイズの単分散ポリスチレン粒子を合成している。これは粒子表面をポリマー鎖が局在化して覆っている、いわゆる機能性粒子である。

第7章では、高分子量ポリ(2-エチル-2-オキサゾリン)鎖を安定化剤とするメタクリル酸メチルの分散重合によるポリマー粒子をつくっている。溶媒はメタノール-水 (70:30重量%) で、粒径分布の狭いミクロンサイズの粒子が得られている。これらの結果は2-オキサゾリンポリマーが工業的に非常に有用な物質であり、ポリマー粒子生産への見通しを明示したものである。

第8章は総括である。

以上要するに本論文は、2-オキサゾリン類の開環重合における新しい手法を開拓し、生成ポリマーの特性を活かして新しい高分子材料を創出したもので、材料化学及びその工業に寄与するところが少なくない。

よって、本論文は工学博士の学位論文として合格と認める。