Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 7129–7136 **7129**
DOI: 10.1021/ma9011895

Organic−Inorganic Hybrid Slide-Ring Gels: Polyrotaxanes Consisting of Poly(dimethylsiloxane) and γ-Cyclodextrin and Subsequent Topological Cross-Linking

Kazuaki Kato,*,† Katsunari Inoue,‡ Masatoshi Kidowaki,† and Kohzo Ito*,†

†*Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan, and* ‡*Advanced Softmaterials Inc., Tokatsu Techno plaza 603, 5-4-6 Kashiwanoha, Kashiwa-shi, Chiba 277-0882, Japan*

Received June 3, 2009; Revised Manuscript Received August 7, 2009

ABSTRACT: A novel polyrotaxane consisting of poly(dimethylsiloxane) (PDMS) and γ-cyclodextrin (γ-CD) is synthesized, and the threaded γ-CDs of polyrotaxane are intermolecularly cross-linked in solution to yield a new class of slide-ring gel. Synthesis of the polyrotaxane is achieved by an end-capping reaction of pseudo-polyrotaxane whose both ends are preliminarily activated as *p*-nitrophenyl ester with *p*-methoxytritylamine derivatives. The obtained polyrotaxane is soluble in *N*,*N*-dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) only in the presence of lithium salts, while PDMS itself is not soluble in these media. Characterization of the polyrotaxane is performed by NMR, FT-IR, and TGA, showing that it is sparsely populated with γ-CDs. Chemical modifications of γ-CDs of the polyrotaxane improve the solubility in various organic solvents and enable further characterizations. An acetylated polyrotaxane is measured by GPC in chloroform to verify the rotaxanation, showing increase of molecular weight and refractive index compared to PDMS. Cross-linking of these polyrotaxanes with and without modifications is carried out with hexamethylene diisocyanate in solution to bridge γ-CDs of the neighboring polyrotaxanes. As a result, an organic−inorganic hybrid slide-ring gel in which PDMS chains are topologically interlocked by figure-of-eight cross-links is materialized after years of the first slide-ring gel consisting of PEG and α-CD reported in 2001.

Introduction

Slide-ring gels, which are cross-linked polyrotaxanes in solution with a unique movable cross-link,[1] have been intensively studied and developed because of the remarkable macroscopic properties, such as high swellability and stretchability.[2] Detailed studies on the mechanical properties have demonstrated that the movable cross-links exhibit obviously distinct behavior from chemical and physical gels, showing J-shape stress−strain curve without hysteresis[3] and biaxial stretching behavior satisfying a neo-Hookean model.[4] Such a novel elastic material shows a large photoinduced deformation mediated by a photosensitive side chain.[5] In the meantime, theoretical studies have explained such unique mechanical behaviors qualitatively with the free junction model that polymer chains can freely slide through the cross-linking junctions.[2] The microscopic sliding has been experimentally verified by small-angle neutron scattering (SANS),[6−9] small-angle X-ray scattering (SAXS),[10] and quasi-elastic light scattering (QELS).[11] Since strong correlations between the macroscopic properties and the nanoscale sliding emerged continuously, fundamental studies on the sliding mode in solution were also intensively investigated in the past few years by using polyrotaxanes.[11−14]

Studies on polyrotaxanes have characterized the sliding phenomena with various chemical techniques after the first report of systematic synthesis of polyrotaxane was reported, based on poly(ethylene glycol) (PEG) and α-cyclodextrin (α-CD).[15] Introductions of degradable end-capping groups to PEG-based polyrotaxanes have demonstrated controlled releases of e.g. α-CD−drug conjugates by an enzyme and by pH change.[16,17] Modifications of the α-CDs with substrates have enhanced multivalent interactions with enzymes because of the high mobility of α-CDs within the mechanically interlocked structure.[18−20] A simple methylation of the α-CDs has induced a thermosensitive sol−gel transition according to aggregations and dispersions of the movable CDs.[21−23] A liquid crystalline polyrotaxane has shown a characteristic dielectric relaxation mode due to the sliding fluctuations of α-CDs.[24,25] A ring-opening polymerization of ε-caprolactone on the α-CDs has afforded a sliding graft copolymer, in which the graft chains can move along the main chain.[26] In this way, most researchers have employed intensively PEG-based polyrotaxanes due to their facile synthesis and established subsequent modifications, in spite of numerous reports on pseudo-polyrotaxane formation with a variety of polymers, including inorganic polymers such as poly(dimethylsiloxane).[27−29]

Inorganic polymer-based polyrotaxanes and the slide-ring materials are worthwhile to be materialized from the perspective of organic−inorganic hybrid materials. Nanoscale mixing of inorganic and organic polymers has been rapidly developed by sol−gel processing utilizing alkoxysilanes.[30−33] Hydrolysis and condensation reactions of trialkoxysilyl compounds were carried out in the presence of preformed organic polymers, affording materials in which inorganic phases (polysiloxanes) were dispersed with the help of noncovalent interactions between both phases such as hydrogen bonds,[34,35] ionic,[36] and $\pi-\pi$ interactions.[37] Covalently bound hybrids have also been prepared from e.g. organic polymers modified with trialkoxysilyl moieties followed by the hydrolysis and condensation.[38−41] In addition to these methods focusing on organic−inorganic interface,

*To whom correspondence should be addressed. E-mail: kato@molle.k.u-tokyo.ac.jp (K.K.), kohzo@molle.k.u-tokyo.ac.jp (K.I.).

Published on Web 08/24/2009

kinetically controlled hybrids in which organic polymers and polysiloxanes are interpenetrating have been materialized by *in situ* polymerizations of organic monomers within the inorganic network[42,43] and by simultaneous formation of both phases.[44−46] All these strategies so far for improving the homogeneity succeeded to afford various novel materials which have flexibility, hardness, transparency, thermostability, and so on.[47−50] Highly oxygen-permeable soft contact lens is a well-known example of hybrid materials consisting of e.g. poly(hydroxyethyl methacrylate) and silicone which provide hydrophilicity and gas permeability, respectively.[51] Rotaxanation between inorganic polymers and organic cyclic molecules is expected to be a fundamental technology for a new class of organic−inorganic hybrid materials. Since the cyclic molecules are topologically bound to the polymer chains, it would be possible that the cyclic molecules disperse within the inorganic polymer networks in an inorganic polymer-based slide-ring gel without macroscopic phase separations. Mesoscale aggregations of CDs observed in several PEG-based slide-ring gels[52] are suggestive of the organic domains dispersed in inorganic networks if we could replace the PEG chain with an inorganic polymer chain.

Changing the main-chain polymer of polyrotaxane, however, is not straightforward because of the diverse characters of polymer chains such as solubility and thickness. Hydrophobic polymers require inhomogeneous complexation with CDs and specific techniques for the subsequent end-capping, while hydrophilic block copolymers such as PPG−PEG−PPG and PEI−PEG−PEI have successfully afforded the polyrotaxanes.[53−58] Solvent-free complexation and end-capping reaction has achieved the production of a polyrotaxane based on poly(tetrahydrofuran) and methylated α-CD.[59,60] One-pot synthesis in DMF including complex formation and subsequent end-capping has afforded a polyrotaxane composed of poly(azomethine) and α- or *β*-CD.[61−63] Poly(propylene glycol)-based polyrotaxane has also been reported.[64,65] Another challenging task is the end-capping of polyrotaxanes composed of "thicker" main-chain polymers and larger CDs. To the best of our knowledge, there are only three examples of *γ*-CD-containing polyrotaxanes: a stilbene-containing polyamine with *β*- and *γ*-CD mixtures,[66] PPG with *γ*-CD,[67] and polyfluorene with *γ*-CD.[68] The latter two polyrotaxanes were obtained by polymerization of a pseudo-polyrotaxane or by copolymerization of a pseudo-rotaxane monomer and a bulky monomer, though these have many joints on their main chains immobilizing *γ*-CDs.

Poly(dimethylsiloxane) (PDMS) is the most versatile inorganic polymer with remarkable properties such as thermostability, good electrical insulation, and high gas permeability. Detailed studies on pseudo-polyrotaxane formations with various molecular weights of PDMS, and α-, *β*-, and *γ*-CDs have shown the efficient complexation only with *γ*-CD at MW > 500,[69,70] though another study has recently reported that with *β*-CD at MW < 3300 and even a subsequent end-capping.[71,72] We report herein synthesis and characterization of a novel polyrotaxane consisting of *γ*-CD and PDMS at first, including the result of GPC obtained with a solubilized polyrotaxane in which hydroxyl groups of *γ*-CDs are chemically modified. We also report successful cross-linking of these silicone-based polyrotaxanes in solution to yield a novel transparent slide-ring gel, in which *γ*-CDs disperse or aggregate to form mesoscale organic domains within the inorganic networks.

Results and Discussion

Complexation between *γ*-CD and PDMS Derivatives. Formation of pseudo-polyrotaxane consisting of *γ*-CD and PDMS chains was induced by ultrasonic agitation in water in accordance with previous reports.[69] White precipitates were obtained from biscarboxypropyl-terminated PDMS (PDMS-BC), which has been determined to have M_n = 10 000 and M_w = 13 700, and from the *p*-nitrophenyl ester (PDMS-BNP), which has M_n = 11 700 and M_w = 14 600 (see Experimental Section). Control experiments with α-CD instead of *γ*-CD showed no precipitate, indicating that the precipitates arose from pseudo-polyrotaxane formations with each PDMS derivative. Turbidity increased slowly according to the pseudo-polyrotaxane formations between *γ*-CD and each PDMS, while shortened controls which have MW = 4600 yielded turbid solutions immediately. To complete the complex formation, each obtained turbid solution was then vigorously stirred at room temperature for 3 days. The turbidity seemed to become constant in 2 days. The obtained precipitates were collected and washed with water repeatedly to remove free CDs and then freeze-dried for the following capping reactions. PDMS chains seemed to be easily extracted from the obtained precipitates with THF, unlike shorter PDMS in the previous reports.[69] Therefore, washing with THF to remove free PDMS-BNP was not carried out to avoid dissociation of the pseudo-polyrotaxane. It is noteworthy that THF extract from the pseudo-polyrotaxane obtained from PDMS-BNP does not contain PDMS-BC as determined by the ^{1}H NMR spectrum (Figure S1), indicating no hydrolysis of the active ester during the complex formation (see Experimental Section and Figure S1 in Supporting Information).

End-Capping Reaction To Produce Polyrotaxane. End-capping reactions of the pseudo-polyrotaxanes were carried out in acetonitrile in the presence of excessive amounts of *p*-methoxytritylamine derivatives as shown in Scheme 1. An unsubstituted trityl group is well-known to be bulky enough for blocking *β*-CD,[73−76] whereas it is still controversial whether it can block *γ*-CD.[77,78] Thus, we designed bulkier stopper amines with *p*-methoxytrityl group and various lengths of methylene linkers. Table 1 shows summary of the end-capping reactions to afford silicone-based polyrotaxanes (SiPR). Production yield and filling ratio (FR) of SiPR became higher with longer methylene linkers of the stoppers at higher reaction temperature. This result indicates that the methylene linkers effectively increase the accessibility of the amino group to the both ends of PDMS enough to prevent unthreading of CDs. Another noticeable difference was found in the reactivity of both ends of PDMS. A pseudo-polyrotaxane prepared as a control from PDMS-BC instead of PDMS-BNP (entry 1 of Table 1) did not produce SiPR by condensation reaction mediated by BOP reagent, which has successfully afforded a polyrotaxane from biscarboxyl (bisamino)-terminated PEG and α-CD capped with a bulky amine (carboxylic acid).[79,80] The reason might be that the reaction intermediate formed by BOP[81,82] is inhibited by *γ*-CD because of the larger cavity than that of α-CD.

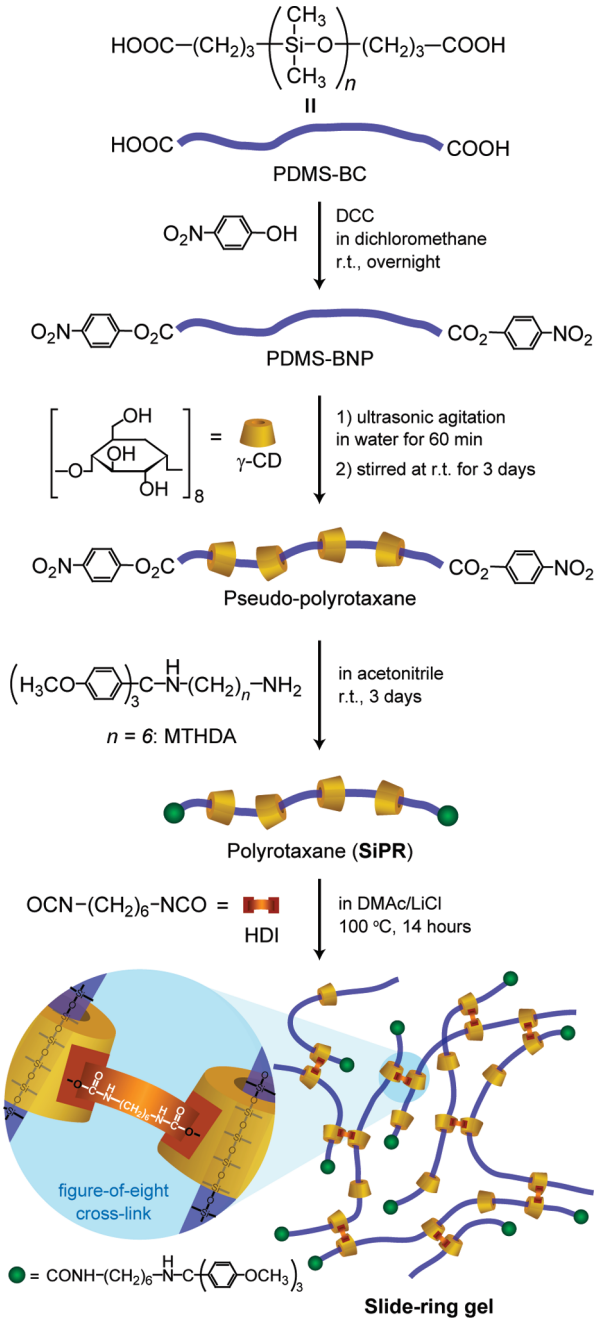
Solvents for the end-capping reaction had a decisive influence on the production of SiPR. Acetonitrile is the best solvent so far, and the yield of SiPR was calculated to be 53% (polymer based) from results of ^{1}H NMR and TGA (see the next section). Similarly, production of the SiPR was also confirmed by the reaction in acetone (data not shown). The pseudo-polyrotaxane was not dissolved in these solvents through the reaction. On the other hand, the reactions in DMF or dichloromethane yielded only trace amounts of SiPR. In the case of reaction in DMF, dissolution of the pseudo-polyrotaxane was observed immediately resulting in a turbid solution, indicating unthreading of *γ*-CD to be dissolved in the solvent. In the case of dichloromethane, PDMS-BNP was extracted from the pseudo-polyrotaxane with the solvent, though the solid of *γ*-CD remains during the reaction. These results indicate that the

Table 1. Yields and Filling Ratios of SiPR Prepared under Various Conditions

entry	PDMS chains	spacer length of stopper amine: *n*	other chemicals[a]	solvent	conditions	yield (%)[b]	FR (%)[c]
1	PDMS-BC	2	BOP, EDIPA	MeCN	RT, 48 h	< 1	
2	PDMS-BNP	2	EDIPA	MeCN	RT, 48 h	15	2
3	PDMS-BNP	4	EDIPA	MeCN	RT, 72 h	21	2
4	PDMS-BNP	4	EDIPA	DMF	RT, 72 h	< 1	
5	PDMS-BNP	4	EDIPA	CH_2Cl_2	RT, 72 h	< 1	
6	PDMS-BNP	6	none	MeCN	RT, 72 h	30	2
7	PDMS-BNP	6	none	MeCN	50 °C, 72 h	53	7

[a] BOP: (benzotriazol-1-yloxy)-tris(dimetylamino)phosphonium hexafluorophosphate. EDIPA: ethyldiisopropylamine. Moler ratio of bulky amine: EDIPA = 1:1.1. [b] Yield based on PDMS. [c] Filling ratio estimated from results of TGA.

Scheme 1. A Synthesis Procedure of SiPR and Slide-Ring Gel Consisting of Poly(dimethylsiloxane) (PDMS) and γ-Cyclodextrin (γ-CD) (DCC: *N,N′*-Dicyclohexylcarbodiimide)



pseudo-polyrotaxane is liable to dissociate in good solvents for either PDMS or γ-CD. In contrast, for the pseudo-polyrotaxane composed of PEG and α-CD, DMF or aqueous solutions have been usually employed for the end-capping reactions in spite of the good solubility for both components, though the reactions have been controlled to be much faster than the unthreading.[27−29] Taken together, selection of poor solvents for both PDMS and γ-CD such as acetonitrile seems to be a key for production of SiPR because of the tendency of easy unthreading in good solvents for either of them.

Table 2. Solubility of SiPR, γ-CD, and PDMS[a]

solvent	SiPR[b]	γ-CD	PDMS[c]
DMF	i	s	i
DMF/LiCl[d]	s	s	i
DMAc	i	s	i
DMAc/LiCl[d]	s	s	i
water	i	s	i
DMSO	i	s	i
CH_2Cl_2	i	i	s
THF	i	i	s
MeCN	i	i	i

[a] Solubility at 20 mg/mL; s = soluble, i = insoluble. [b] Entry 7 of Table 1. [c] Solubility of PDMS-BC and PDMS-BNP; both solubilities seemed to be the same. [d] In the presence of 8 g/100 mL lithium chloride.

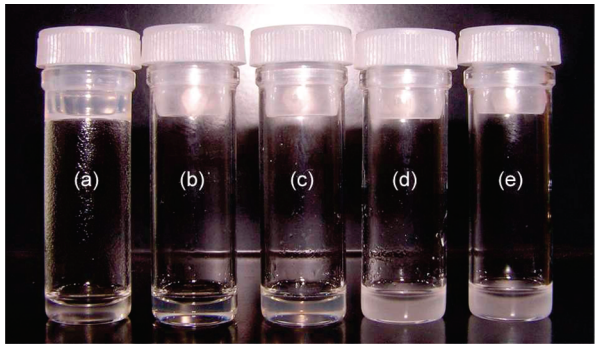


Figure 1. Solubility difference at 20 mg/mL in DMF in the presence and absence of 8 g/100 mL LiCl. (a) SiPR (entry 7 in Table 1) in DMF, (b) SiPR (entry 7) in DMF/LiCl, (c) SiPR (entry 6) in DMF/LiCl, (d) mixture of equal parts of PDMS-BNP and γ-CD in DMF/LiCl, and (e) PDMS-BNP in DMF/LiCl. Many particles of SiPR are insoluble in DMF and stuck on the wall of glass tube (a).

Solubility of Polyrotaxane. Solubility of SiPR obviously differed from that of each component as shown in Table 2, indicating successful end-capping reaction to yield the polyrotaxane. It was found that SiPR with 7% FR (entry 7 of Table 1) is soluble in DMF and DMAc only in the presence of lithium salts as shown in Figure 1. These solvents did not dissolve PDMS-BNP (Figure 1e) but γ-CD. A mixture of γ-CD and PDMS-BNP (Figure 1d) prepared as a control, which has similar contents of both components to the SiPR, clearly showed the difference of solubility arising from the rotaxanation. The solvent systems mediated by lithium ions have previously been found to be effective to dissolve a polyrotaxane consisting of PEG and α-CD.[83] Although DMF and DMAc are good solvents for each component,

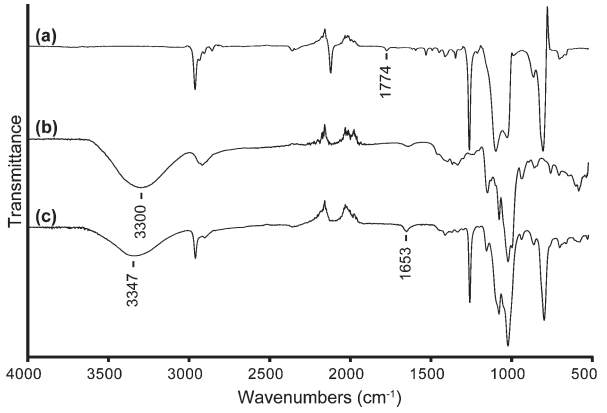


Figure 2. ATR FT-IR spectra of (a) PDMS-BNP, (b) γ-CD, and (c) SiPR. Notable wavenumbers of hydroxyl stretching and carbonyl stretching are described.

the PEG-based polyrotaxane is not dissolved in these solvents. This is because the threaded α-CDs tend to aggregate within the polymer chain and make larger aggregations with the neighboring polyrotaxanes with intra- and intermolecular hydrogen bonds. The hydrogen bonds are interrupted with lithium salts as it has been observed in polysaccharides,[84−88] resulting in dissolution of the polyrotaxane. Therefore, in the same way, SiPR is also thought to be dissolved in the presence of lithium salts by the interruption of hydrogen bonds formed by γ-CDs, strongly supporting the fact of rotaxanation.

On the other hand, SiPR with 2% FR (entry 6 of Table 1) was not very soluble in those solvents (Figure 1c). This result clearly shows that the interruption of intra- and intermolecular hydrogen bonds of SiPR is not enough to explain the dissolutions, unlike PEG-based ones. Insolubility of PEG-based polyrotaxanes is mostly attributed to the aggregations of α-CDs, since various solvents dissolve both components. Several solvents other than the lithium-mediated solvents have been found so far to dissolve PEG-based polyrotaxanes, such as $Ca(SCN)_2$ aqueous solution and ionic liquids.[89,90] It should be noted that all of them are good solvents for both PEG and α-CD. On the other hand, to the best of our knowledge, there is no solvent that dissolve both PDMS and γ-CD. Therefore, it is interesting to investigate the mechanism of solubilization achieved by such small amounts of γ-CDs in the PDMS-based polyrotaxanes, which can cover only 7% of the surface of PDMS, and several measurements for that issue are in progress. Further characterizations, modifications, and cross-linking were performed by using the soluble SiPR (entry 7 of Table 1).

Characterization the Polyrotaxane. FT-IR spectra of SiPR clearly showed the presences of both main components: PDMS and γ-CD as shown in Figure 2, though signals from the capping group were not large enough to be detected. An amide bond as a result of condensation between PDMS-BNP and the capping reagent was observed at 1653 cm^{-1} with disappearance of the *p*-nitrophenyl ester at 1774 cm^{-1}. Hydroxyl stretching of SiPR at 3347 cm^{-1} was shifted from that of γ-CD itself at 3300 cm^{-1}. This might be a result of the interpenetration, since a similar shift was also observed in the pseudo-polyrotaxane (3357 cm^{-1}, data not shown). Figure 3 shows ^1H NMR spectrum of SiPR (2 g/100 mL) measured in DMF-d_7 in the presence of lithium chloride. All signals were assigned to those arisen from PDMS, γ-CD, and the capping group. Besides, the signals of γ-CD were broadened and the broadening remained even in a diluted (0.5 g/100 mL) solution (data now shown). Such broadening has been often

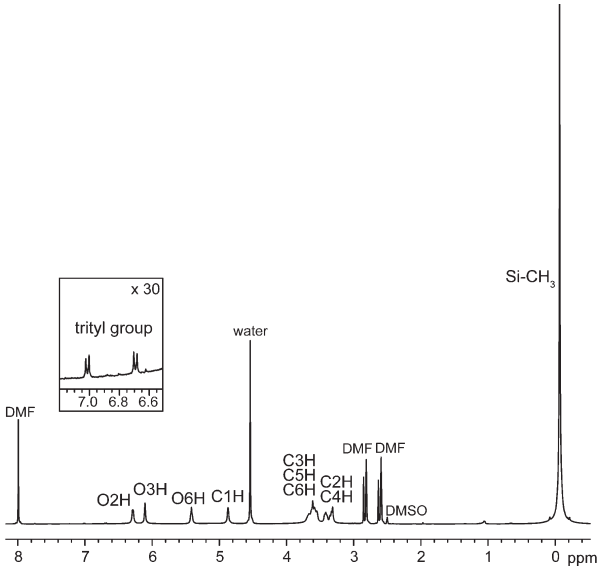


Figure 3. ^1H NMR spectrum (400 MHz, DMF-d_7 in the presence of 8 g/100 mL LiCl, 298 K) of SiPR (entry 7 in Table 1) consisting of γ-CD, PDMS, and *p*-methoxytrityl groups. Reference capillary filled with DMSO-d_6 is attached as a reference.

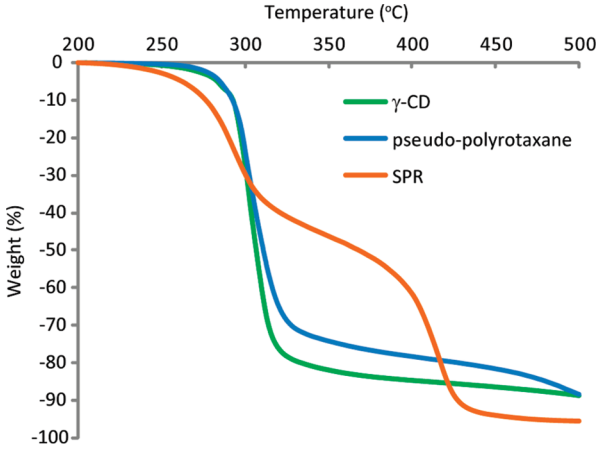


Figure 4. Thermogravimetric analyses of γ-CD, pseudo-polyrotaxane, and SiPR (entry 7 of Table 1). Rate of temperature increase: 5 °C/min, under nitrogen.

regarded as an evidence for rotaxanation in the case of PEG−α-CD polyrotaxanes because it may arise from the decrease in conformational flexibility.[12,91] On the other hand, however, such broadening is not necessary in the case of SiPR and might arise from aggregations or insufficient solubility. On the basis of the ratio of integrations between the methyl proton of PDMS and the methine proton of γ-CD at C1, the filling ratio of γ-CD can be estimated to be 7%, when close packing is defined to be 100%.[69]

The obtained filling ratio was supported by the result of thermogravimetrical analysis, showing two-step decomposition of γ-CD and PDMS at 280 and 410 °C, respectively, with 45:55 ratios by weight as shown in Figure 4. Weight decreases of SiPR before and after 330 °C were regarded as the weights of γ-CD and PDMF, respectively, to estimate the weight ratios. Since the weight ratio between γ-CD and PDMS is about 12*A*:1 when the filling ratio is *A*, the obtained weight ratio from TGA corresponds to $A = 0.07$ (see Experimental Section for the detailed calculation of filling ratios). It is noteworthy that the temperature of decomposition of γ-CD obviously decreased in SiPR compared to that of free γ-CD.

Table 3. Solubility of Modified SiPR[a]

solvent	acetylated SiPR	trimethylsilylated SiPR
DMF	s	i
DMF/LiCl[c]	s	i
DMSO	i	i
THF	i	s
chloroform	s	s
CH_2Cl_2	s	s
toluene	i	s
n-hexane	i	s

[a] Prepared from SiPR of entry 7 in Table 1. Solubility at 20 mg/mL; s = soluble, i = insoluble. [b] In the presence of 8 g/100 mL lithium chloride.

Since the decrease was not observed in the pseudo-polyrotaxane, it might be because the interlocked γ-CDs forms disordered aggregation along the axis polymer, resulting in thermoinstability compared to the crystal of γ-CD. Finally, GPC was carried out in DMF in the presence of lithium chloride with the expectation of the increase of molecular weight due to the rotaxanation. However, no signal was observed except for a small signal that corresponds to trace amounts of γ-CD (data not shown). This might be because an aggregated SiPR was filtered off as the solution passed through a syringe filter (pore size: 0.2 μm) with obvious increase of pressure.

Chemical Modification of Polyrotaxane and Further Characterization by GPC. Chemical modifications of the threaded γ-CDs enabled SiPR to be soluble in various solvents and allowed further characterizations and applications. Hydrophobic substitution of the hydroxyl groups on γ-CD resulted in improvement of the solubility in nonpolar solvents such as chloroform and THF, as shown in Table 3. Since these modifications accommodated the hydrophilic moiety to hydrophobic PDMS, the modified SiPRs might be miscible with such solvents that dissolve PDMS well. Actually, for example, a highly concentrated solution of acetylated SiPR (10 g/100 mL) in chloroform was transparent, and the solutions passed through the syringe filter without pressure increase. The filtrate was diluted and analyzed by GPC to demonstrate the existence of polyrotaxane without aggregations as described in the following paragraph. It is noteworthy that trimethylsilylated SiPR is soluble even in hexane, while PEG-based polyrotaxane has not been solubilized in the apolar solvent by systematically studied chemical modifications.[92] An advantage of PDMS in lipophilicity appears in the solubility of the polyrotaxane.

GPC measurement of the acetylated SiPR was carried out in chloroform, and the elution diagram is shown in Figure 5a. At first, the diagrams show that molecular weight of the acetylated SiPR is apparently much greater than that of PDMS-BNP (Figure 5b). Molecular weight was calculated to be M_n = 38 000 and M_w = 88 000 with a calibration curve prepared by PDMS standards. Such apparent increase of molecular weight has been generally considered to be an evidence of polyrotaxane,[56,93−102] though the obtained molecular weight is not always reliable because of differences in conformation and adsorption condition on the stationary phase between polyrotaxanes and their axis polymer chains. Actually, in this case, the observed molecular weight was obviously larger than that estimated from the filling ratio and acetylation degree obtained from ^{1}H NMR and TGA; MW = 22 800. Besides, at the same time, the diagrams show inversion of refractive index signals; the acetylated polyrotaxane has higher refractive index than chloroform, and PDMS-BNP has a lower one than the solvent. It is reasonable to assume that the refractive index of PDMS increases as a result of rotaxanation with increasing numbers of threaded γ-CD acetylated, which has high refractive index as shown in Figure 5c. Taken together, the main signal at the diagram of Figure 5a can be identified as the polyrotaxane acetylated.

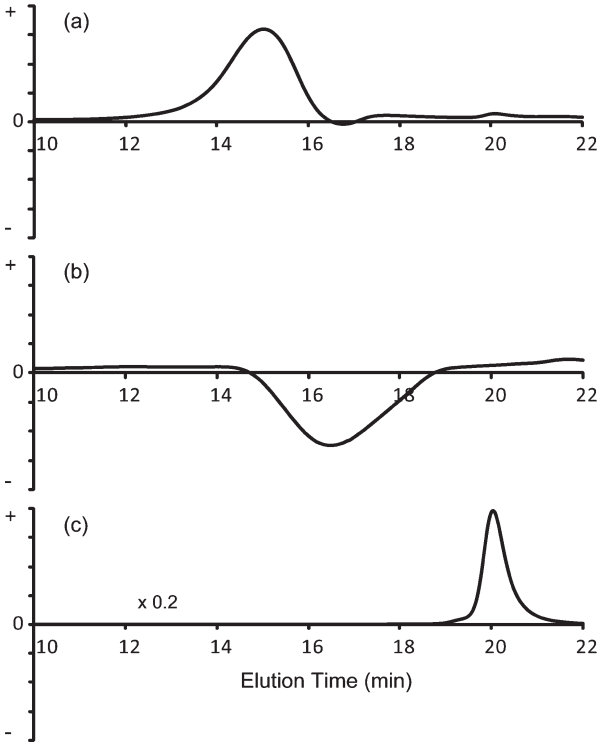


Figure 5. Elution diagrams of (a) acetylated SiPR, (b) PDMS-BNP, and (c) acetylated γ-CD. Column: Shodex GPC K-803 L (0.8 × 30 cm × 2); eluent: chloroform; sample concentration: 2 mg/mL; detection: differential refractive index.

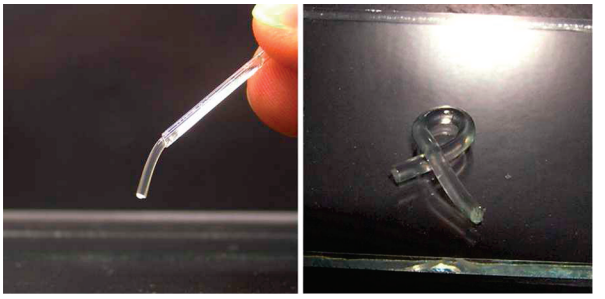


Figure 6. Slide-ring gel prepared from SiPR in DMAc/LiCl. Gelation was carried out in a sealed glass capillary (f = 1.2 mm) at 100 °C for 14 h. Concentrations of SiPR, HDI, and LiCl were 15, 3.5, and 6.4 g/100 mL, respectively.

Cross-Linking of Polyrotaxane To Produce Silicone-Based Slide-Ring Gel. Cross-linking of SiPR was carried out in the solution of DMAc/LiCl to afford an organic−inorganic hybrid slide-ring gel. Hexamethylene diisocyanate (HDI) was employed to cross-link γ-CDs of the neighboring polyrotaxanes selectively as illustrated in Scheme 1. Gelation occurred within an hour at 100 °C in a sealed glass capillary when 15 and 3.5 g/100 mL of SiPR and HDI were used, respectively. To complete the reaction, the gel was removed from the capillary after 14 h. The obtained transparent gel was elastic and flexible enough to be removed from the capillary easily as shown in photographs (Figure 6). γ-CD itself was reacted with HDI in the same condition as a control, and gelation did not occur. Similarly, chemically modified SiPRs were cross-linked in solution to afford

slide-ring gels, though much longer time was required. Solutions of acetylated SiPR in DMF and of trimethylsilylated SiPR in THF afforded gels cross-linked by HDI after 2 and 5 days at 60 °C, respectively. This slow gelation would arise from slow reactions of residual hydroxyl groups of these polyrotaxanes and HDI as a result of steric hindrance induced by substituted groups and decrease of hydroxyl groups available. In this way, γ-CDs of polyrotaxanes were successfully cross-linked with HDI to afford a slide-ring gel in which PDMS chains are topologically interlocked by figure-of-eight cross-links as shown in Scheme 1. This is the first organic−inorganic hybrid slide-ring gel, which is expected to show various unusual properties attributed from the freely movable cross-links combined with remarkable characteristics of silicone such as high gas permeability and good electrical insulation. Transparency of the obtained gels indicates that γ-CDs disperse homogeneously or form mesoscale organic domains in the network of inorganic polymer. Light and X-ray scattering studies to prove the dispersion of organic phase are in progress.

Conclusion

We demonstrated herein that a novel polyrotaxane consisting of PDMS and γ-CD was successfully synthesized and cross-linked subsequently in solution to afford an elastic and transparent gel, in which the inorganic polymer chains were topologically interlocked by figure-of-eight cross-link. This new class of slide-ring gel was materialized by the following key technologies applied: (1) end-capping reaction of an activated pseudo-polyrotaxane with a new bulky stopper in appropriate solvents, (2) solubilization of the obtained polyrotaxane consisting of the lipophilic and hydrophilic moieties by chemical modifications or specific solvents, and (3) optimization of the cross-linking conditions. In particular, the end-capping technology would be applicable for syntheses of other lipophilic polymer-based polyrotaxanes and slide-ring gels. The obtained gels in this study are expected to show unusual mechanical properties arising from the unique cross-linking manner as it has been found in PEG-based slide-ring gels. Besides, from the aspect of organic−inorganic hybrid materials, this material would give us a new strategy for nanoscale mixing of inorganic and organic phases. Rotaxanation and subsequent cross-linking, which are the procedures to obtain slide-ring gels, enable cyclic molecules to disperse within polymer networks with the restrictions of topological bonds. Thus, macroscopic phase separation can be prevented because of the topological restrictions, while aggregations of the cyclic molecules may occur to form micro- or mesoscale domains. The transparent gel obtained through this study demonstrated the utility of this strategy for preparing organic−inorganic hybrid materials. The homogeneity of this material is currently investigated by light scattering studies, and macroscopic properties such as mechanical properties are also in progress.

Experimental Section

Materials. Biscarboxypropyl-terminated PDMS (PDMS-BC) was purchased from Gelest Inc., which has M_n = 10 000 and M_w = 13 700 determined by size exclusion chromatography with a calibration curve prepared by PDMS standards purchased from Polysciences, Inc. The elusion diagram was quite similar to that of PDMS-BNP shown in Figure 5b. A shorter PDMS-BC (MW = 4600) was also purchased from the same company and used only for experiments of complex formation. γ-Cyclodextrin (γ-CD) was purchased from Nihon Shokuhin Kako Co. Ltd. (γ-CD content >98.5%). 4,4′,4″-Trimethoxytrityl chloride and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were from Aldrich. Hexamethylene diisocyanate (HDI), hexamethylenediamine, and *p*-nitrophenol were from TCI. Acetic anhydride was from Kanto Chemical Co., Inc. All dehydrated solvents and other chemicals were purchased from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification.

Measurements. The filling ratio (FR) of SiPR was estimated from various methods such as ^{1}H NMR and TGA based on a definition that 100% of FR means 3:2 molar ratio between monomer unit and γ-CD in which γ-CDs are densely packed along the polymer chain.[69] Thus, the weight ratio between γ-CD and PDMS is (MW of γ-CD) × 2 × *A*:(MW of monomer unit) × 3 ≈ 11.7*A*:1, when the filling ratio is *A*. Therefore, the weight ratios between γ-CD and PDMS of SiPRs with 7% (*A* = 0.07) and 2% (*A* = 0.02) filling ratios are calculated to be 45:55 and 19:81, respectively.

^{1}H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 25 °C. The chemical shift was calibrated using $CHCl_3$ (7.26 ppm) or DMF (8.10 ppm) as internal standards. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet 4700 (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection (ATR) accessory (DurasamplIR II, SensIR Technologies Technologies) in air. Powdered samples were pressed onto a diamond window, and the obtained spectra were analyzed with the spectrometer's OMNIC software. Thermogravimetric analysis (TGA) was performed on Rigaku Thermo Plus Evo with a heating rate of 5 °C/min. Gel permeation chromatography (GPC) was performed on two Shodex GPC K-803 L columns, with chloroform at 40 °C or DMF in the presence of 0.3 M lithium chloride at 50 °C as eluent using RI detection and PDMS standards. Flow rates were 1.0 and 0.4 mL/min for chloroform and DMF/LiCl, respectively.

Preparation of *N*-(*p*-Methoxtrityl)alkylenediamine. *N*-(*p*-Methoxytrityl)alkylenediamine derivatives with different lengths of methylene spacer were similarly synthesized from ethylene-, butylene-, and hexylenediamine by the usual methods.[103,104] A representative procedure for *N*-(*p*-methoxytrityl)hexamethylenediamine (MTHDA) was mentioned as follows. 4,4′,4″-Trimethoxytrityl chloride (10.0 g, 2.72 × 10^{-2} mol) was dissolved in anhydrous dichloromethane (220 mL), and then the solution was slowly dropped into a solution of hexamethylenediamine (50.0 g, 4.30 × 10^{-1} mol) in anhydrous dichloromethane (120 mL) under argon on an ice bath. A white precipitate formed immediately. The resulting slurry was stirred for an hour at 0 °C. The reaction was diluted with dichloromethane (300 mL) and washed with deionized water (3 × 300 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure to afford an orange color oil. The crude product was purified by flash chromatography (silica gel, 90% CH_2Cl_2/7% CH_3OH/3% Et_3N) to give MTHDA as yellow oil; yield: 6.40 g (52%). R_f = 0.33 (90% CH_2Cl_2/7% CH_3OH/3% Et_3N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20−1.50 (m, 8H, 2-CH_2, 3-CH_2, 4-CH_2, 5-CH_2), δ 2.11 (t, 2H, 6-CH_2), δ 2.65, (t, 2H, 1-CH_2), δ 3.78 (s, 9H, CH_3O), δ 6.79 (d, 6H, *m*-Ar), δ 7.34 (d, 6H, *o*-Ar).

Preparation for Active Ester of PDMS. A solution of *p*-nitrophenol (400 mg, 2.88 × 10^{-3} mol) and *N*,*N*′-dicyclohexylcarbodiimide (620 mg, 3.00 × 10^{-3} mol) in anhydrous dichloromethane (12 mL) was added to 3.14 g of PDMS-BC under argon. The reaction solution was stirred at room temperature overnight. Then, the solution was poured into large excess of methanol and centrifuged to precipitate the product. This procedure of reprecipitation was repeated, and then the obtained precipitate was dried under vacuum, affording bis(*p*-nitrophenyl ester)-terminated PDMS (PDMS-BNP) (3.01 g, 2.57 × 10^{-4} mol) as a colorless viscous liquid. ^{1}H NMR ($CDCl_3$): δ 8.27 (d, *m*-Ar), δ 7.27 (d, *o*-Ar), δ 2.63 (t, 3-CH_2), δ 1.81 (m, 2-CH_2), δ 0.66 (t, 1-CH_2), δ 0.07 (s, Si−CH_3). IR (cm^{-1}): 2963 s, 2906 m, 2858 m, 1774 s (C=O stretching), 1531 m, 1449 m, 1413 m, 1348 m, 1262 s, 1098 s, 1028 s, 865 m, 805 s. GPC: M_n = 11 700, M_w = 14 600, M_w/M_n = 1.25.

Complex Formation between γ-CD and PDMS-BNP. PDMS-BNP (2.79 g, 2.38×10^{-4} mol) was charged into a round flask, and an aqueous solution of γ-CD (17.2 g, 1.33×10^{-2} mol, 140 mL) was poured into the flask. The mixture was supersonically agitated for an hour, and then the obtained turbid solution was stirred for 3 days at room temperature. Then, the reaction mixture was centrifuged to precipitate the product. The obtained precipitate was repeatedly washed with deionized water (4 × 200 mL) and then freeze-dried to afford a pseudo-polyrotaxane (16.2 g) as a white solid.

Extraction of PDMS-BNP from Pseudo-Polyrotaxane. DMF (0.3 mL) was added to the obtained pseudo-polyrotaxane (20 mg) and supersonically agitated for a minute to obtain a turbid solution. The solution was poured into dichloromethane (4 mL) to precipitate γ-CD. The precipitate was removed by filtration, and the filtrate was dried under vacuum to afford colorless oil. ^{1}H NMR and IR spectra of the product were almost same as those of PDMS-BNP without the signals arisen from PDMS-BC (see Supporting Information).

Preparation of Polyrotaxane. End-capping reactions were performed in various conditions as shown in Table 1. A representative procedure for SiPR (entry 7 of Table 1) was mentioned as follows. Pseudo-polyrotaxane prepared as mentioned above (10.0 g) was charged in a round flask under argon. MTHDA (3.35 g, 7.47×10^{-3} mol) was dissolved in anhydrous acetonitrile (70 mL), and the solution was poured into the flask charged with the pseudo-polyrotaxane. The reaction mixture was stirred at 50 °C for 3 days under argon. The obtained slurry was centrifuged, and then supernatant was removed. DMF (100 mL) and LiCl (8.00 g) were added to dissolve the obtained precipitate, and then the solution was dropped into dichloromethane (1000 mL) to precipitate the product again. The precipitate was washed with dichloromethane repeatedly (4 × 800 mL) and dried under vacuum to obtain a crude product as a yellow solid. The crude product was again dissolved by adding DMF (100 mL), and the solution was dropped into deionized water (1000 mL) to precipitate the product. The obtained precipitate was repeatedly washed with deionized water (4 × 800 mL) and then freeze-dried. The same procedure of reprecipitation in deionized water was repeated two more times and then freeze-dried to yield SiPR (1.67 g) as a white powder. Yield of SiPR was calculated to be 53% (polymer basis) from the filling ratio obtained by TGA.

Acetylation of SiPR. Procedures of acetylation and trimethylsilylation basically followed those already reported for PEG-based polyrotaxane.[83] Acetylation was carried out as follows. SiPR (30 mg) and *N,N*-dimethyl-4-aminopyridine (2.3 mg, 1.9×10^{-5} mol) were dried under vacuum and then dissolved in anhydrous DMF/LiCl (0.75 mL) (8 g/100 mL of LiCl). Anhydrous pyridine (0.25 mL, 3.1×10^{-3} mol) was added in the solution, followed by the addition of acetic anhydride (0.27 mL, 2.4×10^{-3} mol). The solution was stirred at room temperature overnight. Then, the solution was poured into deionized water (50 mL), followed by centrifugation to obtain a precipitate. The precipitate was repeatedly washed with deionized water and then freeze-dried. Finally, in the same way, the product was purified by reprecipitation also with methanol to yield acetylated SiPR (28 mg) as a white powder. Acetylation degree was calculated to be about 75% based on the integrations of the ^{1}H NMR spectrum with the estimated filling ratio of SiPR obtained as mentioned in the main text. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.6−3.2 (CH and residual OH of γ-CD), 2.1−2.3 (acetyl), 0.07 (PDMS). IR (cm^{-1}): 3524 br (residual OH), 2963 s, 2904 m, 1747 s (C=O stretching), 1369 m, 1261 s, 1079 s, 1027 s, 802 s.

Trimethylsilylation of SiPR. Trimethylsilylation was carried out as follows. SiPR (55 mg) was dispersed in anhydrous DMSO (10 mL), and then 1,1,1,3,3,3-hexamethyldisilazane (700 μL, 3.34×10^{-3} mol) was dropped. The reaction mixture was stirred at 60 °C for 3 h. Then, anhydrous dichloromethane (20 mL) was added to dissolve the precipitate produced and then stirred again for 24 h to complete the reaction. Purification was done by reprecipitation with methanol, followed by washing with methanol repeatedly, to obtain trimethylsilylated SiPR (38 mg) as a white powder. The degree of modification was calculated to be about 70% based on the integrations of the ^{1}H NMR spectrum with an assumption that the hydroxyl group at C6 was completely converted. ^{1}H NMR (ppm in $CDCl_3$): δ 5.2−4.5 (CH at C1 and residual OH at C2 and C3 of γ-CD), δ 4.2−3.2 (other CH of γ-CD), δ 0.19, 0.10 (trimethylsilyl), δ 0.07 (PDMS). IR (cm^{-1}): 3443 br (residual OH), 2962 s, 2903 m, 1412 m, 1365 m, 1262 s, 1094 s, 1042 s, 882 s, 845 s, 806 s.

Cross-Linking of SiPR. 15 mg of SiPR was dissolved in 80 μL of DMAc/LiCl (LiCl: 8 g/100 mL), and then 20 μL of 17.5 g/100 mL HDI solution in DMAc was added into the solution of SiPR. The reaction mixture was stirred and transferred into a glass capillary (inner diameter: 1.2 mm). Then, the capillary was sealed and heated at 100 °C overnight, while the gelation occurred within an hour. The gel was flushed out from the capillary with pressurized air. Acetylated SiPR and trimethylsilylated SiPR also afforded gels under the same conditions, though longer times were required for the gelation. Control experiment was done with γ-CD itself instead of SiPR.

Acknowledgment. This work was partially supported by Grant-in-Aid for Scientific Research ((S), 2008−2012, No. 20221005) and by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Supporting Information Available: ^{1}H NMR spectrum in $CDCl_3$ of the extract from the pseudopolyrotaxane with dichloromethane. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485–487.
(2) Ito, K. *Polym. J.* **2007**, *39*, 489–499.
(3) Okumura, Y.; Ito, K. *Nippon Gomu Kyokaishi* **2003**, 21–26.
(4) Akuzawa, N.; Murata, N.; Urayama, K.; Takigawa, T.; Kidowaki, M.; Ito, K. *Polym. Prepr., Jpn.* **2008**, *57*, 4568–4569.
(5) Sakai, T.; Murayama, H.; Nagano, S.; Takeoka, Y.; Kidowaki, M.; Ito, K.; Seki, T. *Adv. Mater.* **2007**, *19*, 2023–2025.
(6) Karino, T.; Okumura, Y.; Zhao, C.; Kataoka, T.; Ito, K.; Shibayama, M. *Macromolecules* **2005**, *38*, 6161–6167.
(7) Karino, T.; Shibayama, M.; Okumura, Y.; Ito, K. *Physica B* **2006**, *385−386*, 807–809.
(8) Shibayama, M.; Karino, T.; Domon, Y.; Ito, K. *J. Appl. Crystallogr.* **2007**, *40*, S43–S47.
(9) Fleury, G.; Schlatter, G.; Brochon, C.; Travelet, C.; Lapp, A.; Lindner, P.; Hadziioannou, G. *Macromolecules* **2007**, *40*, 535–543.
(10) Shinohara, Y.; Kayashima, K.; Okumura, Y.; Zhao, C.; Ito, K.; Amemiya, Y. *Macromolecules* **2005**, *38*, 6161–6167.
(11) Zhao, C.; Domon, Y.; Okumura, Y.; Okabe, S.; Shibayama, M.; Ito, K. *J. Phys.: Condens. Matter* **2005**, *17*, S2841–S2846.
(12) Zhao, T.; Beckham, H. W. *Macromolecules* **2003**, *36*, 9859–9865.
(13) Karino, T.; Okumura, Y.; Ito, K.; Shibayama, M. *Macromolecules* **2004**, *37*, 6177–6182.
(14) Mayumi, K.; Osaka, N.; Endo, H.; Yokoyama, H.; Sakai, Y.; Shibayama, M.; Ito, K. *Macromolecules* **2008**, *41*, 6480–6485.
(15) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325–327.
(16) Ooya, T.; Yui, N. *J. Controlled Release* **1999**, *58*, 251–269.
(17) Loethen, S.; Ooya, T.; Choi, H. S.; Yui, N.; Thompson, D. H. *Biomacromolecules* **2006**, *7*, 2501–2506.
(18) Ooya, T.; Yui, N. *J. Controlled Release* **2002**, *80*, 219–228.
(19) Ooya, T.; Eguchi, M.; Yui, N. *J. Am. Chem. Soc.* **2003**, *125*, 13016–13017.
(20) Ooya, T.; Utsunomiya, H.; Eguchi, M.; Yui, N. *Bioconjugate Chem.* **2005**, *16*, 62–69.
(21) Karino, T.; Okumura, Y.; Zhao, C.; Kidowaki, M.; Ito, K. *Macromolecules* **2006**, *39*, 9435–9440.
(22) Kataoka, T.; Kidowaki, M.; Zhao, C.; Minamikawa, H.; Shimizu, T.; Ito, K. *J. Phys. Chem. B* **2006**, *110*, 24377–24383.

(23) Kidowaki, M.; Zhao, C.; Kataoka, T.; Ito, K. *Chem. Commun.* **2006**, 4102–4103.
(24) Kidowaki, M.; Nakajima, T.; Araki, J.; Inomata, A.; Ishibashi, H.; Ito, K. *Macromolecules* **2007**, *40*, 6859–6862.
(25) Inomata, A.; Ishibashi, H.; Nakajima, T.; Sakai, Y.; Kidowaki, M.; Shimomura, T.; Ito, K. *Europhys. Lett.* **2007**, *79*, 66004.
(26) Araki, J.; Kataoka, T.; Ito, K. *Soft Matter* **2008**, *4*, 245–249.
(27) Wenz, G.; Han, B.-H.; Muller, A. *Chem. Rev.* **2006**, *106*, 782–817.
(28) Loethen, S.; Kim, J.-M.; Thompson, D. H. *Polym. Rev.* **2007**, *47*, 383–418.
(29) Araki, J.; Ito, K. *Soft Matter* **2007**, *3*, 1456–1473.
(30) Chujo, Y.; Saegusa, T. *Adv. Polym. Sci.* **1992**, *100*, 11–29.
(31) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422–433.
(32) Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010–2027.
(33) Wen, J.; Wilkes, G. L. *Chem. Mater.* **1996**, *8*, 1667–1681.
(34) Saegusa, T. *J. Macromol. Sci. A* **1991**, *28*, 817–829.
(35) Fitzgerald, J. J.; Landry, C. J. T.; Pochan, J. M. *Macromolecules* **1992**, *25*, 3751–3722.
(36) Tamaki, R.; Chujo, Y. *Chem. Mater.* **1999**, *11*, 1719–1726.
(37) Tamaki, R.; Samura, K.; Chujo, Y. *Chem. Commun.* **1998**, 1131–1132.
(38) Huang, H.-H.; Wilkes, G. L. *Polym. Bull.* **1987**, *18*, 455–462.
(39) Noell, J. L. W.; Wilkes, G. L.; Mohanty *J. Appl. Polym. Sci.* **1990**, *40*, 1177–1194.
(40) Chujo, Y.; Ihara, E.; Kure, S.; Suzuki, K.; Saegusa, T. *Makromol. Chem., Macromol. Symp.* **1991**, *42*/*43*, 302–312.
(41) Wei, Y.; Wang, W.; Yeh, J.-M.; Wang, B.; Yang, D.; Murray, J. K. Jr. *Adv. Mater.* **1994**, *6*, 372–374.
(42) Schmidt, H.; Phillip, G. *J. Non-Cryst. Solids* **1984**, *63*, 283–293.
(43) Schmidt, H. *J. Non-Cryst. Solids* **1989**, *112*, 419–423.
(44) Ellsworth, M. W.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 2756–2758.
(45) Novak, B. M.; Davies, C. *Macromolecules* **1991**, *24*, 5481–5483.
(46) Novak, B. M.; Ellsworth, M. W. *Mater. Sci. Eng., A* **1993**, *162*, 257–264.
(47) Philipp, G.; Schmidt, H. *J. Non-Cryst. Solids* **1984**, *63*, 283–292.
(48) Honma, I.; Takeda, T.; Bae, J. M. *Solid State Ionics* **1999**, *120*, 255–264.
(49) Miyata, N.; Fuke, K.; Chen, Q.; Kawashita, M.; Kokubo, T.; Nakamura, T. *Key Eng. Mater.* **2001**, *192*−*195*, 681–684.
(50) Su, C.; Kuraoka, K.; Yazawa, T. *J. Am. Ceram. Soc.* **2001**, *84*, 654–656.
(51) Nicolson, P. C.; Vogt, J. *Biomaterials* **2001**, *22*, 3273–3283.
(52) Shinohara, Y.; Kayashima, K.; Okumura, Y.; Zhao, C.; Ito, K.; Amemiya, Y. *Macromolecules* **2006**, *39*, 7386–7391.
(53) Fujita, H.; Ooya, T.; Kurisawa, M.; Mori, H.; Terano, M.; Yui, N. *Macromol. Rapid Commun.* **1996**, *17*, 509–515.
(54) Fujita, H.; Ooya, T.; Yui, N. *Macromolecules* **1999**, *32*, 2534–2541.
(55) Fujita, H.; Ooya, T.; Yui, N. *Polym. J.* **1999**, *31*, 1099–1104.
(56) Fujita, H.; Ooya, T.; Yui, N. *Macromol. Chem. Phys.* **1999**, *200*, 706–713.
(57) Choi, H. S.; Lee, S. C.; Yamamoto, K.; Yui, N. *Macromolecules* **2005**, *38*, 9878–9881.
(58) Choi, H. S.; Hirasawa, A.; Ooya, T.; Kajihara, D.; Hohsaka, T.; Yui, N. *Chem. Phys. Chem.* **2006**, *7*, 1671–1673.
(59) Kihara, N.; Hinoue, K.; Takata, T. *Macromolecules* **2005**, *38*, 223–226.
(60) Liu, R.; Maeda, T.; Kihara, N.; Harada, A.; Takata, T. *J. Polym. Sci., Part A* **2007**, *45*, 1572–1574.
(61) Simionescu, C. I.; Grigoras, M.; Farcas, A.; Stoleru, A. *Macromol. Chem. Phys.* **1998**, *199*, 1301–1306.
(62) Nepal, D.; Samal, S.; Geckeler, K. E. *Macromolecules* **2003**, *36*, 3800–3802.
(63) Harvath, G.; Nepal, D.; Geckeler, K. E. *Macromol. Rapid Commun.* **2007**, *28*, 2074–2079.
(64) Liu, Y.; Yang, Y.-W.; Chen, Y.; Zou, Y.-W. *Macromolecules* **2005**, *38*, 5838–5840.
(65) Arai, T.; Takata, T. *Chem. Lett.* **2007**, *36*, 418–419.
(66) Herrmann, W.; Schneider, M.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2511–2514.
(67) Okada, M.; Takashima, Y.; Harada, A. *Macromolecules* **2004**, *37*, 7075–7077.
(68) Farcas, A.; Jarroux, N.; Guegan, P.; Harabagiu, V.; Melnig, V. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 3484–3488.
(69) Okumura, H.; Okada, M.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2000**, *33*, 4297–4298.
(70) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2001**, *34*, 6338–6343.
(71) Sukhanova, T. E.; Bronnikov, S. V.; Grigor'ev, A. I.; GubanovaG. N.; Perminova, M. P.; Marangoci, N.; Pinteala, M.; Harabagiu, V.; Simionescu, B. *Russ. J. Appl. Chem.* **2007**, *80*, 1111–1115.
(72) Marangoci, N.; Farcas, A.; Pinteala, M.; Harabagiu, V.; Simionescu, B.; Sukhanova, T.; Bronnikov, S.; Grigoryev, A.; Gubanova, G.; Perminova, M.; Perichaud, A. *High Perform. Polym.* **2008**, *20*, 251–266.
(73) Born, M.; Ritter, H. *Makromol. Chem., Rapid Commun* **1991**, *12*, 471–476.
(74) Noll, O.; Ritter, H. *Macromol. Rapid Commun.* **1997**, *18*, 53–58.
(75) Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Macromolecules* **1997**, *30*, 4288–4294.
(76) Okada, M.; Harada, A. *Org. Lett.* **2004**, *6*, 361–364.
(77) Okada, M.; Kawaguchi, Y.; Okumura, H.; Kamachi, M.; Harada, A. *J. Polym. Sci., Part A* **2000**, *38*, 4839–4849.
(78) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2001**, *34*, 6338–6343.
(79) Tamura, M.; Ueno, A. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 147–154.
(80) Araki, J.; Ito, K. *Macromolecules* **2005**, *38*, 7524–7527.
(81) Castro, B.; Dormoy, J. R.; Evin, G.; Selve, C. *Pept. Proc. Eur. Pept. Symp. 14th* **1976**, 79–84.
(82) Le Nguyen, D.; Castro, B. In *Peptides Chemistry*; Miyazawa, T., Ed.; Protein Research Foundation: Osaka, 1988; p 231.
(83) Araki, J.; Ito, K. *J. Polym. Sci., Part A* **2006**, *44*, 532–538.
(84) Dawsey, T. R.; McCormick, C. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1990**, *C30*, 405–440.
(85) Panar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401–1406.
(86) Terbojevich, M.; Cosani, A.; Conio, G.; Ciferri, A.; Bianchi, E. *Macromolecules* **1985**, *18*, 640–646.
(87) MacCormick, C. L.; Callais, P. A.; Hutchinson, B. H. Jr. *Macromolecules* **1985**, *18*, 2394–2401.
(88) Hasegawa, M.; Isogai, A.; Onabe, F. *J. Chromatogr.* **1993**, *635*, 334–337.
(89) Samitsu, S.; Araki, J.; Kataoka, T.; Ito, K. *J. Polym. Sci., Part B* **2006**, *44*, 1985–1994.
(90) Araki, J.; Kataoka, T.; Ito, K. *J. Appl. Polym. Sci.* **2007**, *105*, 2265–2270.
(91) Ooya, T.; Yui, N. *Biomater. Sci. Polym. Ed.* **1997**, *8*, 437–455.
(92) Araki, J.; Ito, K. *J. Polym. Sci., Part A* **2006**, *44*, 6312–6323.
(93) Harada, A.; Li, J.; Nakamitsu, T.; Kamachi, M. *J. Org. Chem.* **1993**, *58*, 7524–7528.
(94) Harada, A.; Li, J.; Kamachi, M. *J. Am. Chem. Soc.* **1994**, *116*, 3192–3196.
(95) Born, M.; Koch, Th.; Ritter, H. *Acta Polym.* **1994**, *45*, 68–72.
(96) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. W. *Macromolecules* **1997**, *30*, 4807–4813.
(97) Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Macromolecules* **2000**, *33*, 2315–2319.
(98) Jarroux, N.; Guégan, P.; Cheradame, .; Auvray, L. *J. Phys. Chem. B* **2005**, *109*, 23816–23822.
(99) Wollyung, K. M.; Xu, K.; Cochran, M.; Kasko, A. M.; Mattice, W. L.; Wesdemiotis, C.; Pugh, C. *Macromolecules* **2005**, *38*, 2574–2586.
(100) Ooya, T.; Ito, A.; Yui, N. *Macromol. Biosci.* **2005**, *5*, 379–383.
(101) Choi, H. S.; Ooya, T.; Yui, N. *Macromol. Biosci.* **2006**, *6*, 420–424.
(102) Takata, T.; Kohsaka, Y.; Konishi, G. *Chem. Lett.* **2007**, *36*, 292–293.
(103) Tilley, J. W.; Levitan, P.; Kierstead, R. W. *J. Med. Chem.* **1980**, *23*, 1387–1392.
(104) Sottofattori, E.; Anzaldi, M.; Balbi, A.; Artali, R.; Bombieri, G. *Helv. Chim. Acta* **2002**, *85*, 1698–1705.