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Preparation of mechanically cross-linked poly(vinyl alcohol)

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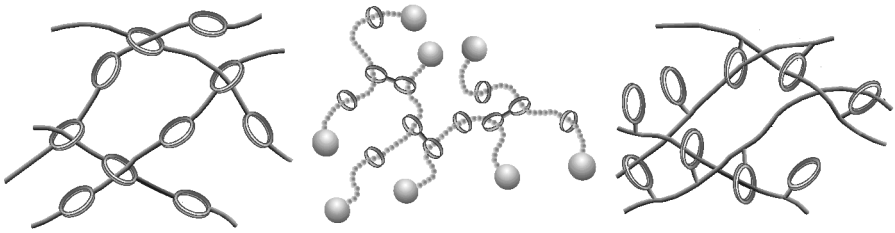
Summary

A novel cyclic macromonomer based on a cyclic polystyrene was prepared. Its radical copolymerization with vinyl acetate was carried out to give a mechanically cross-linked poly(vinyl acetate) which was converted to a mechanically cross-linked poly(vinyl alcohol) with high swellability.

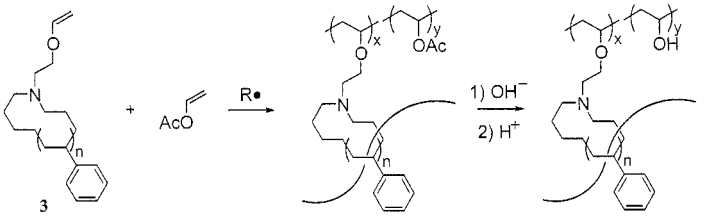
Introduction

Mechanically cross-linked polymers have received attention as a new class of soft materials carrying mobile cross-linking (Scheme 1). It has been shown that mechanically cross-linked vinyl polymers were prepared by radical copolymerizations of vinyl monomers with monomers which possess macrocyclic moieties [1-5]. The threading of a main chain trough the macrocyclic cavity of another chain leads to the formation of network structure.



Scheme 1. Mechanically Cross-Linked Polymers

We have reported a cyclic macromonomer based on a cyclic polystyrene to provide mechanically cross-linked poly(*tert*-butyl acrylate) and polystyrenes [6,7]. As part of our efforts to exploit a new series of mechanically cross-linked polymers, we report a preparation of mechanically cross-linked poly(vinyl alcohol). We prepared a novel resonance-unstabilized cyclic macromonomer **3** based on a cyclic polystyrene. Radical copolymerization of the cyclic macromonomer **3** with vinyl acetate was carried out to obtain a mechanically cross-linked poly(vinyl acetate) which was successfully converted to a mechanically cross-linked poly(vinyl alcohol) with good swelling property (Scheme 2).



Scheme 2. Preparation of Mechanically Cross-Linked Poly(vinyl alcohol)

Experimental

Materials

Cyclic polystyrenes **1** and **2** were prepared according to the previously reported method [6]. Vinyl acetate (Wako) was freshly distilled before use. Benzoyl peroxide (BPO) (Nacalai Tesque) was dissolved in a small amount of chloroform and precipitated by adding an equal volume of methanol. 2,2'-Azobis(isobutyronitrile) (AIBN) (Nacalai Tesque) was recrystallized from ethanol. 2,2'-Azobis(2,4-dimethylvaleronitrile) (V-65) (Wako) was used as received. Solvents and other reagents were purified by usual methods.

Instruments

Infrared spectra were recorded on a Jasco IR-700 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-EX270 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G2500H and G3000H columns using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively. Matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF MS) was performed using a Shimadzu Kompact II spectrometer using dithranol and silver trifluoromethanesulfonate as a matrix and ionization reagent, respectively.

Synthesis of Cyclic Macromonomer (3)

A mixture of cyclic polystyrene (**2**) (M_n = 2600, M_w/M_n = 1.03) (0.64 g, 0.3 mmol), 2-chloroethyl vinyl ether (68 mg, 0.6 mmol), K_2CO_3 (0.22 g, 1.6 mmol), and *N,N*-dimethylformamide (DMF) (8 mL) was stirred at 80 °C for 48 h. The reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water, died over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using chloroform as the eluent. After the first band was collected to remove the excess 2-chloroethyl vinyl ether, the eluent was changed to isopropyl ether and the second band was collected to give 0.34 g (54%) of **3** as a white powder. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.2-6.3 (phenyls and CH=), 4.2 (=CH_2), 4.0 (=CH_2), 3.7 (OCH_2), 2.9 (NCH_2), 2.3-0.8 (CH and CH_2). MALDI-TOF MS analysis: M_n = 2740 (M_w/M_n = 1.05).

*Solution Copolymerization of **3** with VAc*

A mixture of cyclic macromonomer **3** or cyclic polystyrene **1**, vinyl acetate (VAc), initiator, and benzene was placed in a glass ampule that was degassed completely by the freeze-thaw method and sealed. The ampule was placed in a bath for the time of polymerization. The reaction mixture was poured into an excess of diethyl ether and washed well with diethyl ether. The obtained polymer was soaked in a large excess of methanol to extract the unlinked polymers. Then the swollen gel was placed under reduced pressure to remove the solvents to obtain a mechanically cross-linked poly(vinyl acetate).

*Emulsion Copolymerization of **3** with VAc*

A mixture of VAc, cyclic macromonomer **3**, sodium stearate, potassium persulfate, and 1% solution of poly(vinyl alcohol) (PVAL) was placed in a round-bottom glass flask. The system was purged with nitrogen to remove the dissolved air and heated at 70 °C for 12 h with magnetic stirring. The reaction mixture was poured into an excess of methanol to obtain a mechanically cross-linked poly(vinyl acetate).

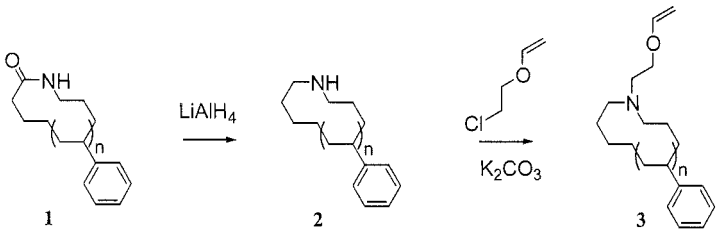
Synthesis of Mechanically Cross-Linked Poly(vinyl alcohol)

A 0.5 mL of 40% NaOH solution was added to a mixture of mechanically cross-linked poly(vinyl acetate) (obtained from run 3 in Table 2) (0.20 g) and methanol (10 mL). The reaction mixture was stirred at room temperature for 12 h. It was poured into an excess of methanol and washed well with methanol to obtain 0.10 g (quant) of a mechanically cross-linked poly(vinyl alcohol) as a pale yellow solid.

Results and Discussion

*Synthesis of Cyclic Macromonomer (**3**)*

Our idea is to polymerize a resonance-unstabilized macromonomer **3** with vinyl acetate in order to introduce a sufficient amount of **3** unit into a polymer chain. The cyclic macromonomer **3** was prepared according to Scheme 3 using a well-defined cyclic polystyrene **1** as a starting material. In order to introduce a non-stabilized polymerizable group, condensation of **2** with 2-chloroethyl vinyl ether was carried out in DMF using K_2CO_3 as a base.



Scheme 3. Preparation of Cyclic Macromonomer **3**.

The ^{1}H NMR spectrum of **3** is shown in Figure 1. In addition to the signals due to polystyrene, vinyl protons were observed at 4.2 and 4.0 ppm. The evidence for the structure **3** was confirmed by MALDI-TOF MS as shown in Figure 2. Each peak in the spectrum represents a cyclic macromonomer **3** which was ionized with the attachment of Ag^+. The spacing between peaks was 104.1 Da, corresponding to the molar mass of styrene. The observed peak masses were in good agreement with the calculated values for the proposed structure **3**.

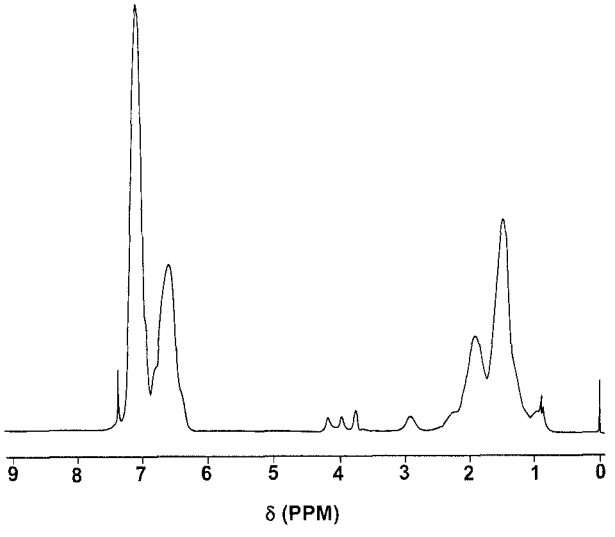


Figure 1. ^{1}H NMR of cyclic macromonomer **3** in $CDCl_3$.

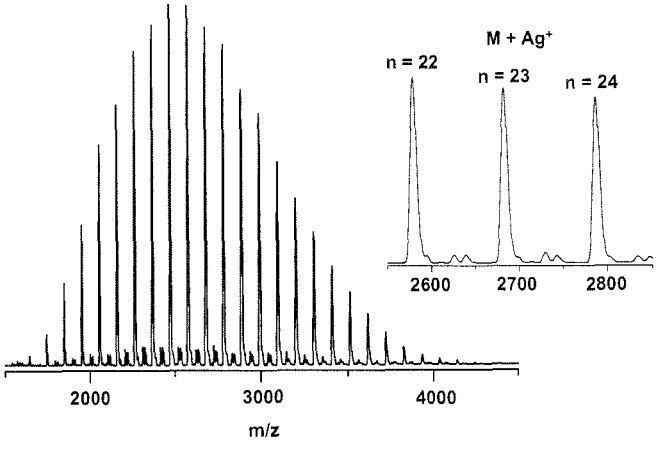


Figure 2. MALDI-TOF MS of cyclic macromonomer **3**.

*Copolymerization of **3** with VAc*

Radical copolymerizations of cyclic macromonomer **3** with vinyl acetate (VAc) in solution state were carried out at various temperatures. The polymerization results are summarized in Table 1. Soluble polymers were obtained in the absence of cyclic macromonomer **3** (runs 1, 3, and 5). On the other hand, insoluble polymers were obtained in runs 2, 4, and 6. These insoluble polymers correspond to mechanically cross-linked poly(vinyl acetate) due to the threading of cyclic polystyrene moiety by a segment of another polymer chain.

Table 1. Radical Copolymerizations[a] of Cyclic Macromonomer **3** with VAc

					MeOH-insoluble part	MeOH-soluble part	
run	initiator	[**3**]/[VAc]	temp., °C	time, h	%	%	M_n[c]
1	BPO	0	80	10	0	95	47,000
2	BPO	1/1200	80	10	7	82	24,000
3	AIBN	0	60	84	0	95	49,000
4	AIBN	1/1200	60	84	11	70	29,000
5	V-65[b]	0	50	12	0	72	82,000
6	V-65[b]	1/1200	50	12	22	46	33,000
7	V-65[b]	1/1200[d]	50	12	0	79	48,000

[a] Conditions: VAc = 1.0 g, [VAc]/[initiator] = 400, Benzene = 0.5 mL. [b] 2,2'-Azobis(2,4-dimethylvaleronitrile). [c] Determined by GPC as polystyrene standard. [d] Cyclic polystyrene **1** was used instead of **3**.

It is known that the radical polymerization of vinyl acetate in solution gives relatively short and branched polymers due to chain transfer reactions. Actually, the molecular weight of the copolymerization product decreased by adding the cyclic macromonomer. This may be indicative of the chain transfer reaction to the macromonomer. Hence, radical polymerization of vinyl acetate in the presence of unfunctionalized cyclic polystyrene **1** (parent polymer of **3**) was carried out as a control experiment (run 7). Figure 3 showed GPC eluograms of the reaction products obtained from run 7. It exhibited a small peak which absorbs in the UV region at 254 nm. The molecular weight of the peak top (M_n = 2200) is close to that of **1** (M_n = 2600). The molecular weight of the high molecular weight fraction (48,000) was lower than that of the product obtained from run 5 (82,000). These experimental results indicate a chain transfer reaction to the cyclic polystyrene.

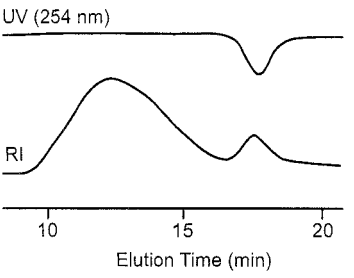


Figure 3. GPC eluograms of reaction product obtained from run 7 with RI and UV detections.

The yield of the methanol-insoluble part increased with decrease of polymerization temperature. Further, the molecular weight of the MeOH-soluble part increased with decrease of polymerization temperature due to the suppression of chain transfer reaction. The more the cyclic unit **3** in a polymer chain, the more the yield of the mechanically cross-linked polymer.
Hence, we carried out emulsion polymerization to improve the gel yield. The polymerization results are summarized in Table 2.

Table 2. Emulsion Copolymerizations[a] of Cyclic Macromonomer **3** with VAc

				MeOH-insoluble part	MeOH-soluble part	
run	[**3**]/[VAc]	temp., °C	time, h	%	%	M_n[b]
1	0	70	12	0	99	149,000
2	1/1800	70	12	16	76	104,000
3	1/1200	70	12	49	51	105,000

[a] Conditions: VAc = 1.0 g, $K_2S_2O_8$ = 3 mg, $C_{12}H_{25}OSO_3Na$ = 100 mg, 1% PVAL = 5 mL.
[b] Determined by GPC as polystyrene standard.

The molecular weight of the MeOH-soluble part (over 100,000) was much higher than those obtained in solution polymerization. Although emulsion polymerization technique improved the chance of chain threading for network formation, the gel yield was ca. 50%. The copolymerization ratios may account for the modest yield. For M_1 as 2-chloroethyl vinyl ether and M_2 as vinyl acetate in radical copolymerization, r_1 and r_2 are reported to be 0.16 and 2.36, respectively [8], suggesting that the cyclic macromonomer **3** was reluctant to participate in the copolymerization.

Mechanically Cross-Linked Poly(vinyl alcohol)

Finally, the mechanically cross-linked poly(vinyl acetate) was subject to base-catalyzed hydrolysis to obtain mechanically cross-linked poly(vinyl alcohol). Figure 4 shows IR spectra of mechanically cross-linked poly(vinyl acetate) and poly (vinyl alcohol). Mechanically cross-linked poly(vinyl alcohol) no longer exhibited carbonyl peak at 1700 cm^{-1}. Instead, a broad peak appeared around 3400 cm^{-1}, indicating the complete conversion of poly (vinyl acetate) to poly(vinyl alcohol).

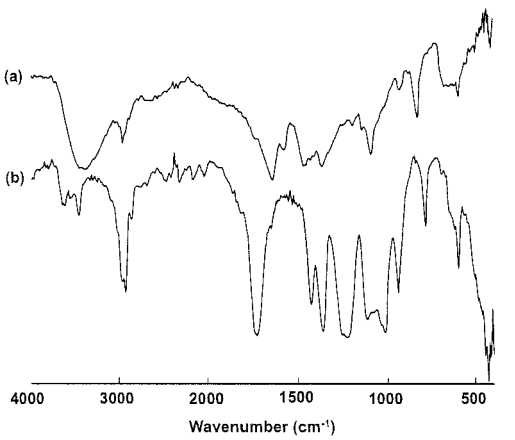


Figure 4. IR spectra of Mechanically cross-linked (a) poly(vinyl alcohol) and (b) poly(vinyl acetate).

Swelling Property

The swelling property of the mechanically cross-linked poly(vinyl alcohol) was evaluated by soaking the sample in THF and water. The volumes of the swollen cross-linked poly(vinyl alcohol)s are given in Table 3, together with the values of chemically cross-linked poly(vinyl alcohol) using glutaraldehyde as a cross-linking agent.

Table 3. Swelling Volume (mL/g) of Cross-Linked Poly(vinyl alcohol)

	solvent	
type of cross-linking	THF	water
mechanical[a]	12	11
chemical[b]	5.0	4.1

[a] Obtained from run 3 (Table 2). [b] Cross-linked with 1 mol% glutaraldehyde.

It is clear that the mechanically cross-linked poly(vinyl alcohol) exhibited higher swelling volumes than those of chemically cross-linked one, probably due to a very low cross-linking level and an easy movement of polymer chain.

Conclusions

We demonstrated a novel cross-linking of poly(vinyl alcohol) using a cyclic macromonomer as a nonbonding cross-linking agent. A number of poly(vinyl alcohol) hydrogels have been prepared by freezing/thawing process, radiation cross-linking, and chemical cross-linking [10]. Mechanical cross-linking of poly(vinyl alcohol) is expected to exhibit novel mechanical and biomedical properties.

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