Noncovalent Cross-Linking of Poly(methyl methacrylate) via Polypseudorotaxane

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ABSTRACT: Free radical bulk polymerization of methyl methacrylate (MMA) was carried out in the presence of a macrocyclic amine based on cyclic polystyrene. The polymer changed to an insoluble solid upon heating at 180 °C in a vacuum. The insolubility is attributed to the *in situ* formation of a polypseudorotaxane, followed by the covalent fixation of the threaded ring segment with the linear chain to form a noncovalent three-dimensional structure.

Introduction

In recent years, a novel concept has been introduced to achieve noncovalent network polymers utilizing movable cross-linking (mechanical cross-linking) (Scheme 1.)[1–6] This class of materials has attracted a great deal of interest as new functional materials with unusual chemical, physical and mechanical properties due to the high degrees of freedom in segmental movement since no chemical bonding exists between polymer chains.[7–10] There are several synthetic methods to introduce noncovalent cross-linking into polymer networks depending on the type of three-dimensional structure. A versatile methodology for noncovalent cross-linked vinyl polymers involves copolymerization of vinyl monomers with cyclic macromonomers (Scheme 2.)[11–17] The network structure is formed by the threading of the cyclic moiety by a segment of another polymer chain during the polymerization process. However, the drawback of this method is lack of processability. The resulting network polymers precipitate from the reaction system, making it difficult to process these materials homogeneously into shaped articles.

We propose a novel synthetic strategy for preparation of noncovalent cross-linked polymer. The strategy is based on two-step curing reactions as shown in Scheme 3. The first step is to prepare a polypseudorotaxane as a prepolymer by free radical polymerization of a vinyl monomer in the presence of a large ring molecule. Polypseudorotaxanes represent a new class of macromolecular architectures in which macrocycles are penetrated by linear polymers and thus the two components are mechanically linked with each other.[18–22] Threading can occur during polymerization in the presence of a macrocycle.[23–26] The second step corresponds to the conversion of the polypseudorotaxane to noncovalent cross-linked structure by solid-state fixation of the linear chain with rings (both threaded and free). Since polypseudorotaxanes are tractable precursor polymers, it is possible to obtain cross-linked polymers with desired shapes. In this present paper *in situ* preparation of a polypseudorotaxane composed of polystyrene-based macrocyclic amine with poly(methyl methacrylate) (PMMA) and its conversion to a noncovalent cross-linked network by a solid-state thermal amidation reaction are reported.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded at room temperature on a JEOL EX-270 nuclear magnetic resonance spectrometer. Samples were dissolved in $CDCl_3$ and tetramethylsilane (TMS) was used as the internal standard. Infrared spectra were recorded on a Jasco FT/IR-4100 infrared spectrophotometer. Gel permeation chromatography (GPC) was carried out on a Tosoh HLC-8020 chromatograph equipped with polystyrene gel columns (Tosoh TSK gel Multipore H_{XL}-M; exclusion limit = 2×10^6; 300 × 7.5 mm) and refractive/ultraviolet dual mode detectors. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using polystyrene standards. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI−TOF MS) was performed with a Shimadzu Kompact II spectrometer in the linear mode with an acceleration voltage of 20 kV. The sample solution was prepared by the dissolution of polymer (1 mg) in 1 mL of THF. The matrix solution was prepared by the dissolution of dithranol (23 mg) in 1 mL of THF. Matrix and polymer solutions were mixed in a 1/1 ratio. To aid sample ionization, the MALDI target was prespotted with 0.5 μL of a 0.1 mmol/mL solution of silver trifluoromethanesulfonate in THF and allowed to dry at room temperature. A 0.5−1.0 μL aliquot of the polymer/matrix mixture was deposited on top of ionization agent and air-dried. Photoluminescence spectra were recorded on a Hamamatsu photonic multichannel analyzer PMA-11 with exciting wavelength of 365 nm.

Materials. Polystyrene-based macrocyclic amide **1** and macrocyclic amine **2** were prepared according to the previously reported procedure.[27] Methyl methacrylate (MMA) was dried over CaH_2, distilled under reduced pressure, and stored under a nitrogen atmosphere at −16 °C. All other chemicals were of reagent grade and used as received.

Reaction of Dihexylamine with Methyl Stearate at 80 °C. Dihexylamine (93 mg, 0.50 mmol) and methyl stearate (149 mg, 0.50 mmol) were dissolved in 4 mL of benzene and heated at 80 °C for 12 h. The reaction mixture was placed under reduced pressure to remove the solvent, and a colorless oil (240 mg) was obtained.

Reaction of Dihexylamine with Methyl Stearate at 180 °C. A mixture of dihexylamine (93 mg, 0.50 mmol) and methyl stearate (149 mg, 0.50 mmol) was heated at 180 °C for 12 h under a stream of nitrogen and an orange oil (230 mg) was obtained.

Prepolymers P1−P3. Prepolymers **P1−P3** were synthesized by free radical bulk polymerizations of MMA in the presence of macrocyclic amine **2**. A typical procedure is described as following. A mixture of **2** (M_n = 2400) (120 mg, 0.05 mmol), MMA (0.5 g, 5 mmol), and benzoyl peroxide (BPO) (8 mg) was placed in an ampule that was degassed completely by the freeze−thaw method and sealed. The ampule was placed in a bath at 70 °C for 12 h. The polymer was soaked in a large excess of methanol for 48 h to extract the unreacted monomers and dried at room temperature in a vacuum for 12 h to give 0.59 g (95%) of **P2** as colorless semitransparent solid. GPC: M_w = 483 kDa; PDI = 1.9.

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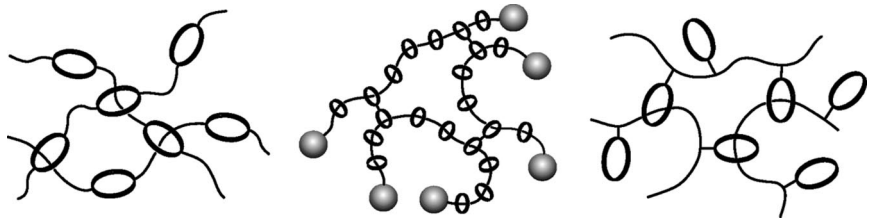
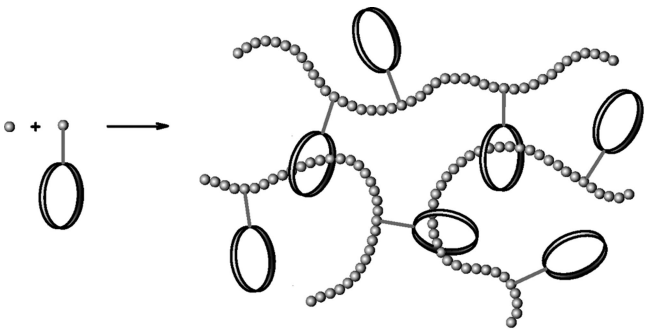
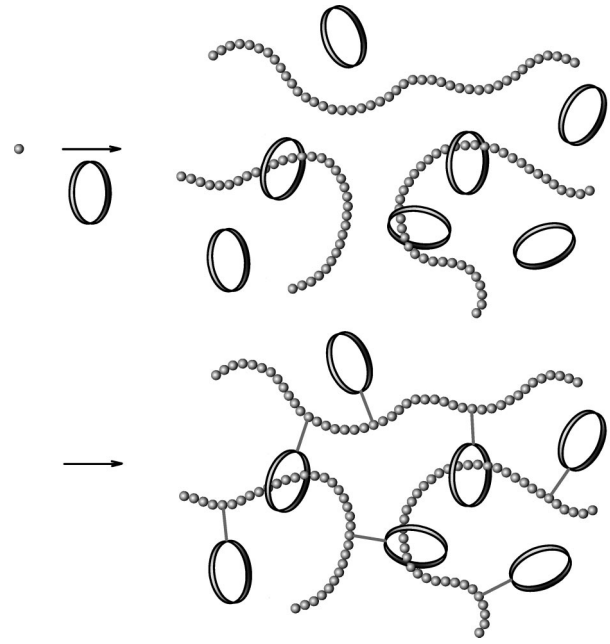
Scheme 1. Examples of Noncovalent Cross-Linked Polymers



Scheme 2. Noncovalent Cross-Linking Using Cyclic Macromonomer



Scheme 3. Noncovalent Cross-Linking via Polypseudorotaxane



Prepolymer P4. A mixture of **1** (M_n = 2400) (120 mg, 0.05 mmol), MMA (0.5 g, 5 mmol), and BPO (8 mg) was placed in an ampule that was degassed completely by the freeze−thaw method and sealed. The ampule was placed in a bath at 70 °C for 12 h. The polymer was soaked in a large excess of methanol for 48 h to extract the unreacted monomers and dried at room temperature in a vacuum for 12 h to give 0.60 g (97%) of **P4** as a colorless semitransparent solid. GPC: M_w = 589 kDa; PDI = 1.5.

Prepolymer P5. A homogeneous mixture of macrocyclic amine **2** (M_n = 2400) (24 mg, 0.01 mmol) and commercially available PMMA (Aldrich, typical M_w 350 kDa, 50 mg) was prepared by grinding gently in a mortar.

Noncovalent Cross-Linking by Heat Treatment. A 50 mg portion of the prepolymer was heated at 180 °C in a vacuum and soaked in a large excess of THF for 48 h. The swollen gel was taken and placed under reduced pressure to remove the volatile materials. Three sample tests were performed for each cross-linking, and data were averaged.

Swelling Property. The swelling property of the noncovalent cross-linked gel was evaluated by soaking a sample in THF at room temperature for 24 h. The percentage swelling was calculated according to the following relationship:[28]

$$\% \text{ swelling} = (w_s - w_d)/w_d \times 100$$

where w_s and w_d are the weight of swollen gel and of dry gel, respectively.

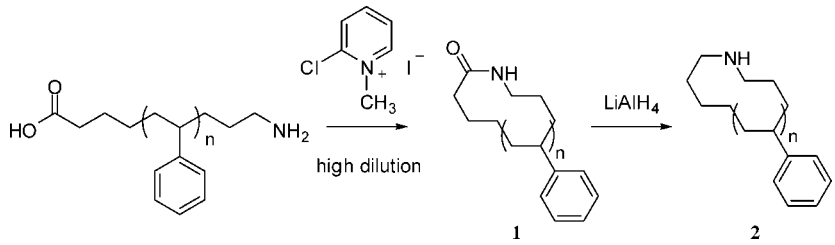
Results and Discussion

Macrocyclic Amine 2. In this work, we used a well-defined cyclic polystyrene **2** bearing an amino group as a ring segment for polypseudorotaxane. The polymer **2** was prepared from α-carboxyl, ω-amino heterodifunctional polystyrene in two steps according to Scheme 4. Figure 1 shows MALDI−TOF MS of the macrocyclic amine **2** used in this study. The spectrum exhibited the presence of only one peak series. Each peak in the spectrum represents a macrocyclic amine **2**, which was ionized by the attachment of silver ion during the MALDI process. The number-average molecular weight and molecular weight distribution were determined to be 2400 and 1.02, respectively. It is a ring of, on average, ca. 60 atoms and large enough for linear chains to thread through.[29–32] The amino group of **2** is a useful functional group for construction of noncovalent network structures. The nucleophilic attack of the amine at the carbon atom of an ester attached to a linear chain gives an amide linkage, which will lead to a noncovalent three-dimensional network.

Model Reaction. For the successful noncovalent cross-linking of PMMA by two-step curing, the reactivity between the amine and ester functionalities should meet the following requirements: (1) must be low under radical polymerization conditions (inert in the polypseudorotaxane formation) and (2) must be high enough to form an amide linkage at elevated temperature. The model reaction between methyl stearate and dihexylamine was examined. We chose methyl stearate (bp 181−182 °C/4 mmHg) and dihexylamine (bp 192−195 °C) as model compounds for PMMA and macrocyclic amine **2**, respectively, because they are not volatile at 180 °C. To check the reactivity in free radical conditions, methyl stearate was mixed with dihexylamine in benzene and heated at 80 °C for 24 h. The reaction mixture still contained unreacted materials (Figure 2a.) On the other hand, the reaction products obtained at elevated temperature at 180 °C showed new peaks at 3.3−3.1 ppm corresponding to methylene protons adjacent to the amide nitrogen (Figure 2b). The conversion was estimated to be 55% from the integral ratios. These experimental results suggest that the combination of PMMA and macrocyclic amine **2** will provide a system capable of two-step curing for noncovalent cross-linking.

Preparation of Prepolymers. Three prepolymers, **P1**−**P3**, were prepared by free radical bulk polymerization of MMA in the presence of a macrocyclic amine **2** at various [**2**]/[MMA] ratios. These prepolymers were obtained in almost quantitative yield and were completely soluble in THF. The polymerization results are summarized in Table 1. In addition, we prepared

Scheme 4. Preparation of Macrocyclic Amine 2



prepolymers **P4** and **P5** for control experiments. Prepolymer **P4** is a polypseudorotaxane composed of PMMA and cyclic polystyrene without amine functionality. It was prepared by radical polymerization of MMA in the presence of a macrocyclic amide **1** instead of **2**. Prepolymer **P5** is a physical blend (unthreaded mixture) of macrocyclic amine **2** and preformed PMMA.

We examined prepolymer **P2** (obtained from entry 2, Table 1) by GPC with a dual detection system consisting of UV (254 nm) and RI detectors as shown in Figure 3. The GPC curve showed two fractions. The lower molecular weight fraction corresponds to free macrocyclic amine **2** which can be detected by both RI and UV detectors. The polymer at the higher molecular weight region is the linear chain composed of PMMA. Interestingly, this fraction can be detected by the UV detector although PMMA has no absorption at 254 nm. This is probably due to the fact that some macrocyclic amine still remain in the threaded state.

Since NMR spectroscopy will reveal information about threading,[33–35] prepolymers **P1**−**P5** were analyzed by ^{1}H NMR in $CDCl_3$ solution. Although we could not find any characteristic signals of the threaded cyclic polystyrene in the region from 2.0 to 1.0 ppm assignable to the methine and methylene protons due to the broad backbone signals of the PMMA chain, polypseudorotaxane formation was indicated from phenyl protons. Figure 4 shows partial ^{1}H NMR spectra of prepolymers **P1**−**P5** and macrocyclic amine **2**. The phenyl protons due to polystyrene show two absorption peaks around 7.1 and 6.6 ppm. In the case of **P1**−**P4**, the higher field signal centered at 6.6 ppm split into two portions, indicating different chemical environment for the styrene unit. Splitting at 6.6 ppm was not observed for macrocyclic amine **2** and prepolymer **P5** (unthreaded mixture of macrocyclic amine and PMMA). From these results the splitting of the signal at 6.6 ppm could be related to the cyclic polystyrene threaded by PMMA chain.

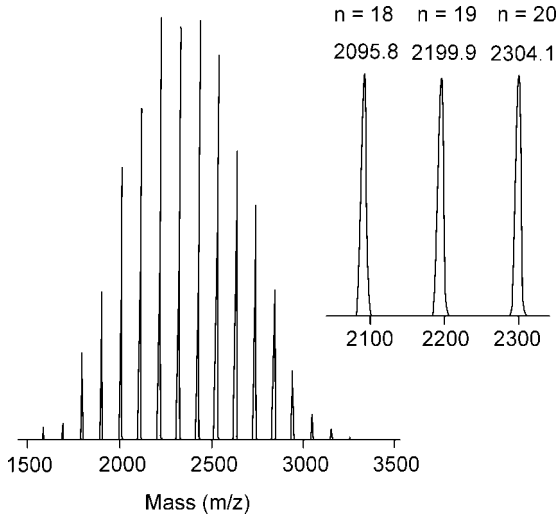


Figure 1. MALDI−TOF MS of **2** used in this study. The masses correspond to silver adducts.

Further evidence for polypseudorotaxane formation is provided by emission spectra.[36,37] Figure 5 shows photoluminescence spectra of prepolymers **P1**−**P3**, **P5**, and macrocyclic amine **2** in the solid state. The λ_{em} of the macrocyclic amine **2** is observed at 440 nm due to the polystyrene backbone. A red shift in the emission maximum is observed for **P1**−**P3** and the λ_{em} shifts to a longer wavelength with increase of macrocyclic amine content. On the other hand, the emission of prepolymer **P5** is quite similar to that of **2**. These results indicate these shifts observed for **P1**−**P3** in the emission maxima can be attributed to the interaction between threaded cyclic polystyrene and PMMA chain, which results in a red shift of the emission maxima.

Noncovalent Cross-Linking of PMMA. Prepolymers **P1**−**P3** were subjected to heat treatment at 180 °C in a vacuum.

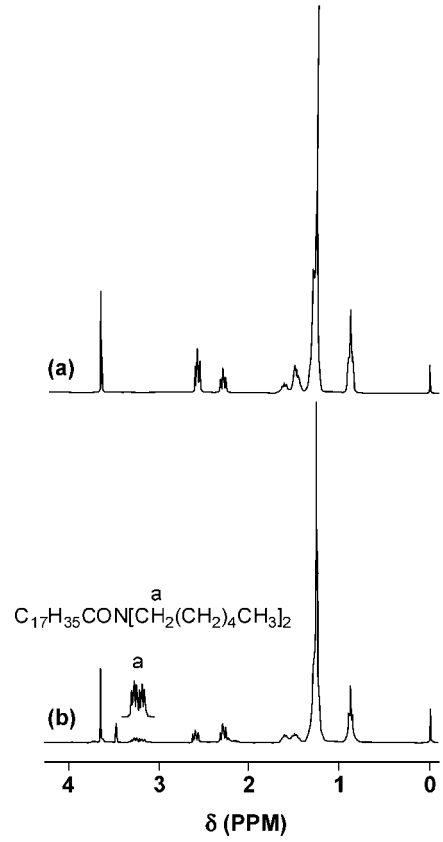


Figure 2. ^{1}H NMR spectra of the reaction mixture prepared from dihexylamine and methyl stearate at (a) 80 °C and (b) 180 °C.

Table 1. Preparations[a] of Prepolymers P1−P3

entry	prepolymer	MMA, g (mmol)	**2**, mg (mmol)	[**2**]/[MMA]	yield, g (%)	M_w, kDa	PDI
1	**P1**	0.50 (5.0)	60 (0.025)	1/200	0.53 (94)	488	1.8
2	**P2**	0.50 (5.0)	120 (0.05)	1/100	0.59 (95)	483	1.9
3	**P3**	0.50 (5.0)	240 (0.1)	1/50	0.72 (97)	491	1.8

[a] Conditions: BPO = 8 mg, temp = 70 °C, time = 12 h.

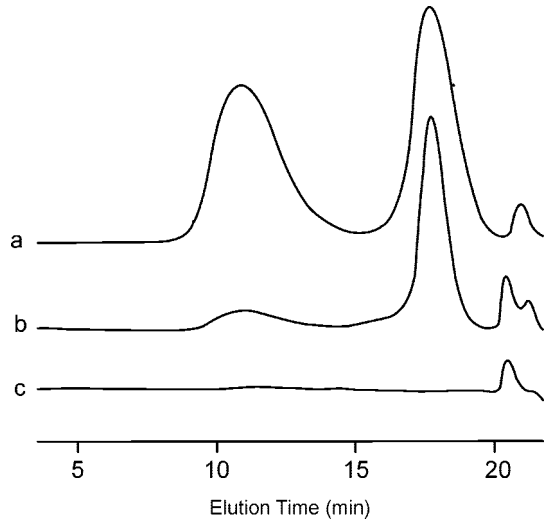


Figure 3. GPC traces of (a) prepolymer **P2** (RI), (b) prepolymer **P2** (UV), and (c) PMMA used for **P5** (UV).

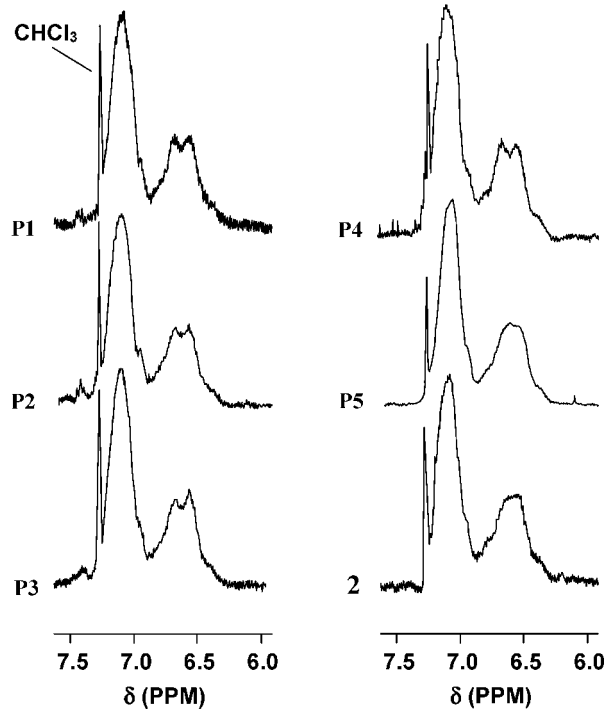


Figure 4. Partial ^{1}H NMR spectra (270 MHz) of solutions ($CDCl_3$) containing prepolymers **P1**−**P5** and macrocyclic amine **2**.

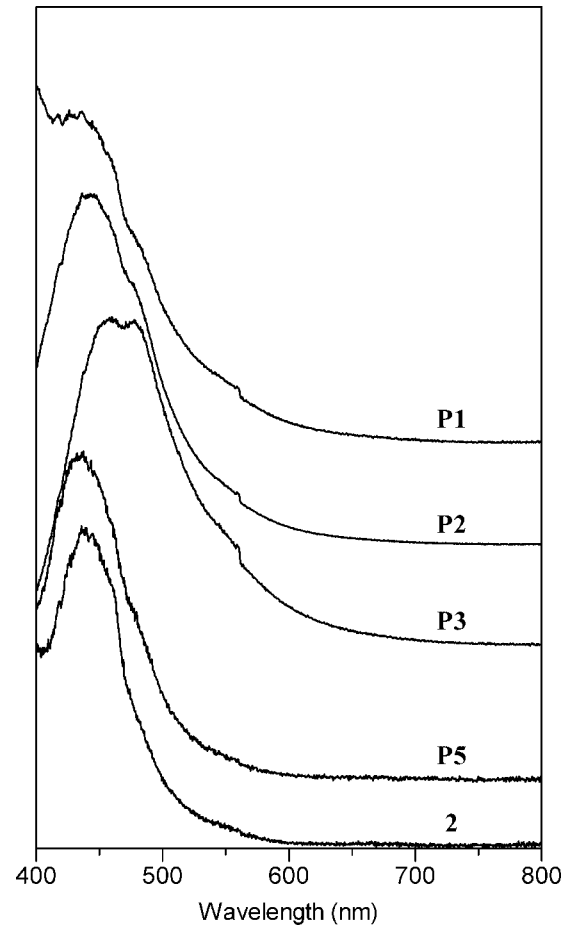


Figure 5. Photoluminescence spectra of prepolymers **P1**−**P3**, **P5**, and macrocyclic amine **2** in the solid state.

Table 2. Heat Treatment of Prepolymers P1−P5 at 180 °C

				THF-insoluble part	
entry	prepolymer	time, h	THF-soluble part (%)	%	% swelling
1	**P1**	4	100	0	
2	**P1**	8	83	17	4100
3	**P1**	24	45	55	2400
4	**P2**	4	5	95	1500
5	**P2**	8	4	96	820
6	**P2**	24	6	94	800
7	**P3**	4	9	91	1200
8	**P3**	8	6	94	600
9	**P3**	24	4	96	560
10	**P4**	24	100	0	
11	**P5**	24	100	0	

The results of the heat treatment are summarized in Table 2. In the case of prepolymer **P1** ([**2**]/[MMA] = 1/200), the product heated for 4 h dissolved slowly, but completely in THF which indicated that no appreciable cross-linking had taken place at this stage (entry 1). Longer reaction times were needed for gelation (entries 2 and 3). On the other hand, prepolymers **P2** ([**2**]/[MMA] = 1/100) and **P3** ([**2**]/[MMA] = 1/50) displayed a marked tendency toward gelation. Cross-linked polymers were obtained in more than 90% yield within 4 h of reaction (entries 4 and 7). This is because incorporation of large amount of ring segment favors the threading by the linear chain.

The swelling property of the gel was found to be significantly dependent upon both macrocyclic amine content and reaction time. Higher amounts of macrocyclic amine and longer heating time gave lower percent swelling. This is reasonably explained by the amount of the amide linkage formed during the thermal curing. One would expect the number of amide linkages to increase, resulting in higher network density in the PMMA gel.

The formation of the amide linkage was supported by IR results. Figure 6 displays the IR spectra of the prepolymer **P2** before and after heat treatment. After heat treatment, a new peak at 1633 cm^{-1} due to amide carbonyl group was observed, indicating that cross-linking took place by the nucleophilic attack of macrocyclic amine at the carbonyl group of PMMA to form an amide linkage.

Control Experiments. Both prepolymers **P4** and **P5** remained soluble in THF after heating at 180 °C in a vacuum for 24 h (entries 10 and 11, Table 2). No significant changes are observed in molecular weight, indicating that side reactions such as covalent cross-linking by chain transfer reactions are not responsible for the gelation. These control experiments support the gelation mechanism depicted in Scheme 5.

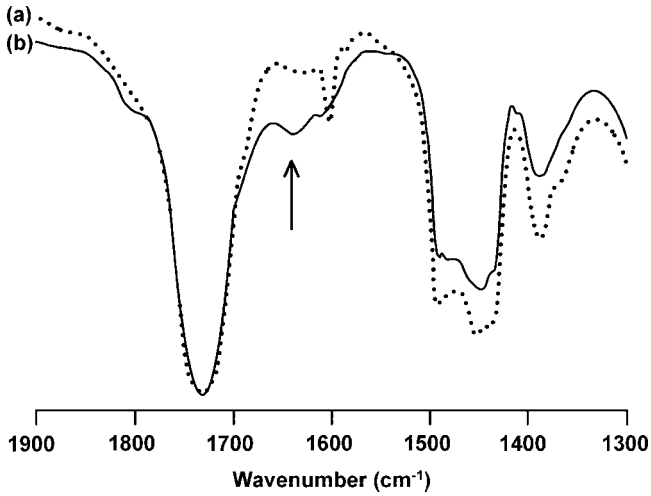
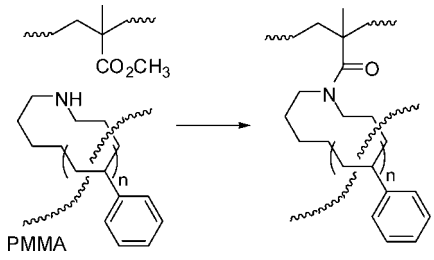


Figure 6. IR spectra of KBr pellet samples of (a) prepolymer **P2** and (b) the product after heat treatment at 180 °C.

Scheme 5. Gelation Mechanism



Conclusions

We have demonstrated a novel synthetic pathway for a noncovalent network of PMMA. The synthetic procedure involves *in situ* formation of a polypseudorotaxane by free radical polymerization of MMA in the presence of a macrocyclic amine. Evidence for a polypseudorotaxane formation is indicated by GPC, ^{1}H NMR, and photoluminescence measurements. Although the amount of the threaded macrocycles (threading efficiency) remains obscure at this stage, it appears that the large size of macrocyclic amine based on cyclic polystyrene (ca. 60 atoms on average) is favorable for threading. By utilizing the solid-state thermal amidation reaction of the polypseudorotaxane, the covalent fixation of the threaded ring with linear chain results in noncovalent cross-linking to form a three-dimensional network.

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