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Tailored Synthesis of Star and Network Poly(dimethylsiloxane)s through Electrostatic Self-Assembly and Subsequent Covalent Fixation of Telechelics Having Cyclic Onium Salt Groups[†]

Yasuyuki Tezuka*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Tomio Iwase and Tomoo Shiomi

Department of Material Science and Technology, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-21, Japan

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ABSTRACT: Efficient electrostatic self-assembly and subsequent covalent fixation of macromolecules by multipoint interaction have been achieved with poly(dimethylsiloxane), poly(DMS), having five-membered cyclic ammonium salt end groups. Thus a 1-methylpyrrolidinium salt end group was introduced at a single or both chain ends of poly(DMS) (**1** and **1′**, respectively). The anion-exchange reaction of **1** and **1′** with di-, tri- and tetracarboxylates was found to take place efficiently by a simple precipitation of **1** and **1′** into aqueous solution containing an equimolar amount of carboxylate compounds (thus ca. 10^{-3} M, 0.01−0.1 wt % concentration). The subsequent heat treatment of ionically-assembled products at 120 °C caused covalent fixation by the selective ring opening reaction of cyclic onium salt groups by nucleophilic attack of carboxylate anion, to produce star and model-network poly(DMS) structures in high yields.

Introduction

Construction of supramolecular architectures through a self-assembly process is of an intensive current interest from both academic and industrial viewpoints.[1] A variety of noncovalent intermolecular forces may be applied to cause an efficient self-assembly of molecular building blocks. Hydrophobic as well as van der Waals forces are operating typically in cyclodextrin systems.[2] Also hydrogen-bonding[3] and metal−ligand coordination forces[4] are applicable to form unique self-assembly structures, since they are more specific and directional than hydrophobic or van der Waals forces. A dipole−dipole attraction of π-donor and π-acceptor reagents is another efficient driving force to achieve topologically unique supramolecular arcitectures, such as rotaxanes and catenanes.[5,6]

Coulombic interaction is a long-range attractive or repulsive force, which may also be utilized to construct supramolecular assemblies. Inorganic and organic crystallites are consequence of electrostatic attractive forces operating between ionic species. Since the Coulombic force is inversely proportional to a dielectric constant of the medium, most crystallites are intractable in organic media of low dielectric constants. On the other hand, organic salts containing macromolecular, hydrophobic moieties may offer a unique opportunity to provide attractive interaction between ion pairs to cause efficient association in organic medium or in bulk. This principle has been industrially exploited for ionomer materials.[7] Surface manipulation to create unique wetting−dewetting, friction−lubrication properties by specific and directional alignment of macromolecules at surfaces through Coulombic interaction is also of increasing interest.[8−10]

In the present paper, we report on a novel self-assembly process utilizing a Coulombic interaction between cationic end groups of hydrophobic, water-insoluble macromolecules and plurifunctional anionic carboxylate groups in an aqueous phase at the surface of macromolecules components.[11−15] Highly efficient association has been achieved between cationic and anionic groups located on separate molecules (one positioned at the end of a linear, hydrophobic macromolecule and another in a hydrophilic small molecule). Furthermore, the self-assembled product, which is connected through a Coulombic attractive force operating between a cyclic ammonium cation at the polymer chain end and a carboxylate counteranion, has been transformed to one with a permanent linkage by a covalent fixation reaction. In this process, a nucleophilic ring opening reaction of cyclic onium salt groups has been utilized with a carboxylate counteranion at an elevated temperature.

Experimental Section

Reagents. Telechelic poly(dimethylsiloxane) having a pyrrolidinium salt at either one or both ends (**1** and **1′**) were prepared by the method detailed before.[16−19] Plurifunctional carboxylates used in the present study were sodium benzoate, sodium terephthalate, and sodium and lithium salts of trimesic acid and pyrromelitic acid. They were either purchased or prepared by the standard neutralization method with sodium or lithium hydroxides.[20] Deionized water (chromatography grade, Nacalai Tesque) was used as received.

Procedures. Into an ice-cooled 100 mL aqueous solution containing a prescribed amount of plurifunctional carboxylate compound, a THF solution of an equimolar amount of **1** or **1′** (0.5 g in 5.0 mL of THF), with respect to the ionic groups, was added dropwise by a syringe under vigorous stirring. The resulting turbid solution turned gradually clear, and the precipitate adhered to the wall of the beaker. The stirring was continued for a further 3 h, and the product was recovered by decanting the solvent. The products from both **1** and **1′** remained soluble, and they were isolated by freeze-drying from benzene solution. The isolated products from both **1** and **1′** were then subjected to a heat treatment at 120 °C for 24 h.

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* To whom correspondence should be addressed.

[†] This paper is dedicated to Professor Eric Goethals in honor of his 60th birthday.

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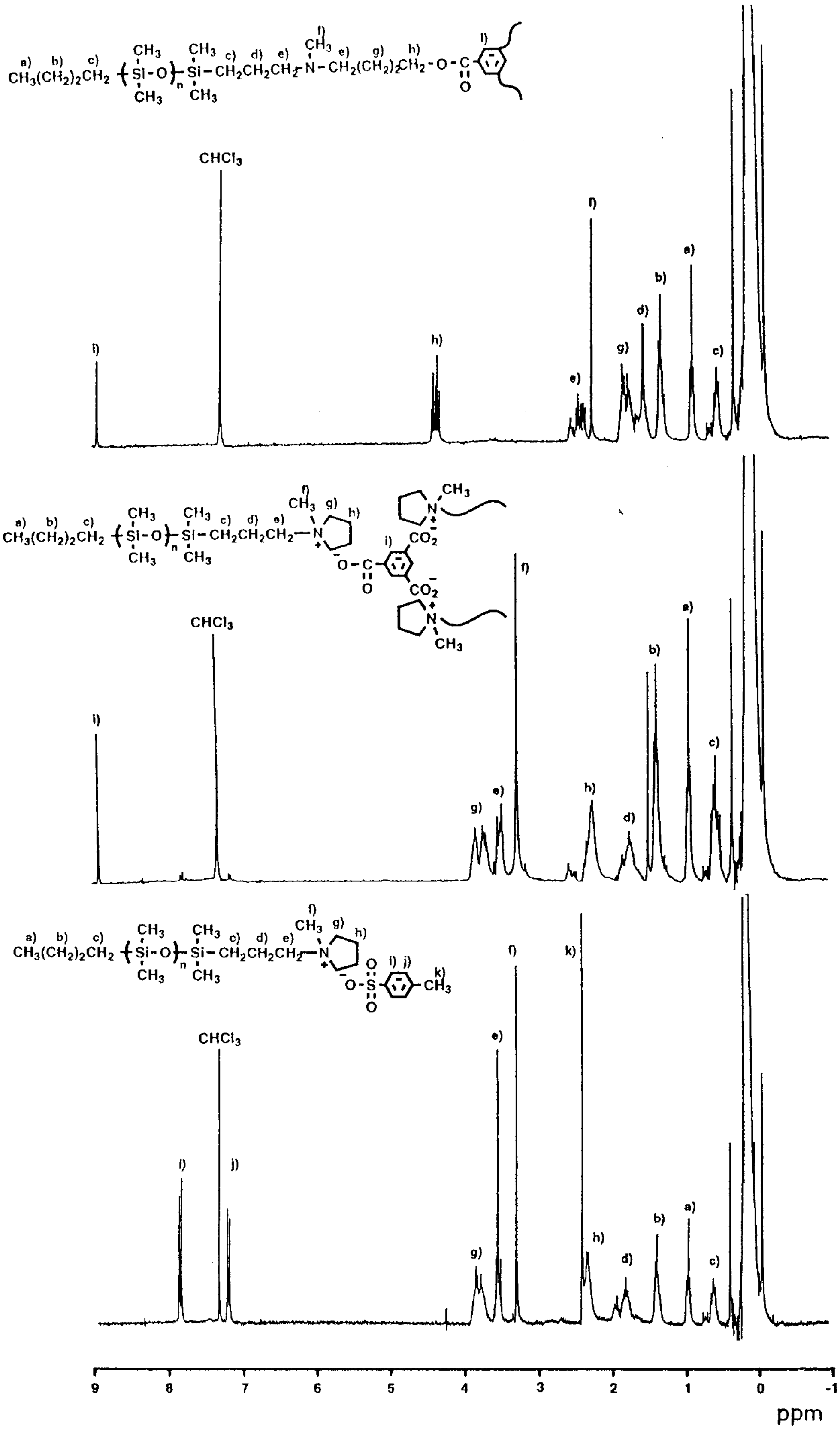

Figure 1. 270 MHz ^{1}H-NMR spectra of **1** (bottom) and the coupling product with a tricarboxylate before (middle) and after (top) the heat treatment at 120 °C. (Sample: run 2 in Table 1, $CDCl_3$, 40 °C).

An insoluble, but swollen, gel product was obtained from **1′**, and was subjected to a Soxhlet extraction with THF for 24 h to estimate the gel content.

Measurements. The 270 MHz ^{1}H-NMR spectra were recorded on a JEOL JNM-GX 270 apparatus at 40 °C in $CDCl_3$. Chemical shift values were referenced from the residual protonated solvent in $CDCl_3$ ($\delta = 7.30$). IR spectra were taken on a SHIMADZU FT-IR 8100 apparatus (40 or 60 scans) using a cast film sample on a NaCl plate from a chloroform solution. GPC measurements were performed using a Tosoh HLC-8020 (an RI detector is preinstalled) with additional UV detector, Model UV 8000, at 254 nm and a conductivity detector, Model

Table 1. Coupling Reaction between Telechelic Poly(DMS) Having Pyrrolidinium Salt Groups (1 and 1′) and Pluricarboxylates[a]

	telechelic poly(DMS)						
run	type	$M_n \times 10^{-3}$ (GPC)	pluricarboxylate (functionality)	recovd yield (%)	ion-exchange[b] yield (%)	product[c] yield (%)	swelling[d] degree (%)
1	**1**	4.1	terephthalate, Na (2)	98	99	100	*e*
2	**1**	4.1	trimesate, Li (3)	96	99	99	*e*
3	**1**	4.1	pyrromelitate, Li (4)	100	65	57	*e*
4	**1′**	5.8	terephthalate, Na (2)	99	99	100	*e*
5	**1′**	5.8	trimesate, Li (3)	99	99	98	28.2
6	**1′**	5.8	pyrromelitate, Li (4)	100	90	97	12.8
7	**1′**	9.1	terephthalate, Na (2)	99	100	100	*e*
8	**1′**	9.1	trimesate, Li (3)	99	92	93	45.5
9	**1′**	9.1	pyrromelitate, Li (4)	99	89	94	27.4

[a] **1** or **1′** (0.5 g) in 5.0 mL of THF was precipitated into 100 mL of aqueous solution containing an equimolar amount (with respect to ionic groups) of pluricarboxylate, 0 °C, 3 h. [b] By ^{1}H-NMR. [c] Runs 1–3, star polymer yield by GPC; runs 4–9, gel content, after the heat treatment at 120 °C for 24 h. [d] In THF, 25 °C. [e] No gelation.

CM 8010. A column system of TSK G3000HXL and TSK G4000HXL was used either in a separate mode or in a connected mode with THF as eluent at a flow rate of 1.0 mL/min. The degree of swelling (by weight) for a series of poly(DMS) network products was determined by measuring the weights of the dry network and the swollen network samples immersed in THF at 25 °C for 24 h.

Results and Discussion

Mono- and bifunctional poly(dimethylsiloxane)s, poly(DMS)s, having pyrrolidinium salt end groups (**1** and **1′**, respectively) were prepared by sequential end-group transformation from hydroxyl groups with tosylation and subsequently with quaternization by *N*-methylpyrrolidine.

The anion-exchange reaction of **1** or **1′** was performed with plurifunctional carboxylates by a simple addition of a THF solution of **1** or **1′** into an aqueous solution containing an equimolar ionic quantity of plurifunctional carboxylate. The precipitated product, which adhered to the wall of the beaker, was isolated and was subsequently subjected to a heat treatment at 120 °C for 24 h.

^{1}H-NMR spectra of the product between **1** and trifunctional carboxylate before and after the heat treatment are shown in Figure 1. The ion-exchange reaction from tosylate to tricarboxylate anion was confirmed by the complete replacement of the tosylate signal at 2.40, 7.82, and 7.16 ppm by the benzene tricarboxylate signal at 8.94 ppm visible as a singlet peak. The signal intensity of the latter protons was measured to be close to one-third of that of the pyrrolidinium *N*-methyl protons, indicating that most of three carboxylate groups reacted. To our surprise, this ion-exchange reaction proceeded efficiently despite the very low overall concentration of carboxylate, i.e. ca. 10^{-3} M, (0.01–0.1 wt %), with an equivalent quantity to the cyclic onium salt group in **1**. A long-range attractive interaction between the ionic species in polymer chain ends and in the carboxylate salts at the polymer precipitate/aqueous solution interface is presumed to promote the local aggregation of ionic groups to achieve high efficiency in this ion-exchange reaction.

The addition of an increased amount of carboxylate compound in the system, on the other hand, caused the partial elimination reaction of the pyrrolidinium salt end groups of poly(DMS). Such an elimination reaction of the salt end groups on poly(DMS) was observed previously,[21] where the back-biting type, nucleophilic attack of a base or alkaline species took place toward the siloxane bond in the vicinity of the end groups. The lithium salts of tri- and tetrafunctional carboxylates are preferred over their sodium salt counterparts in order to achieve higher ion-exchange yields and to avoid the elimination reaction of end groups in **1**.

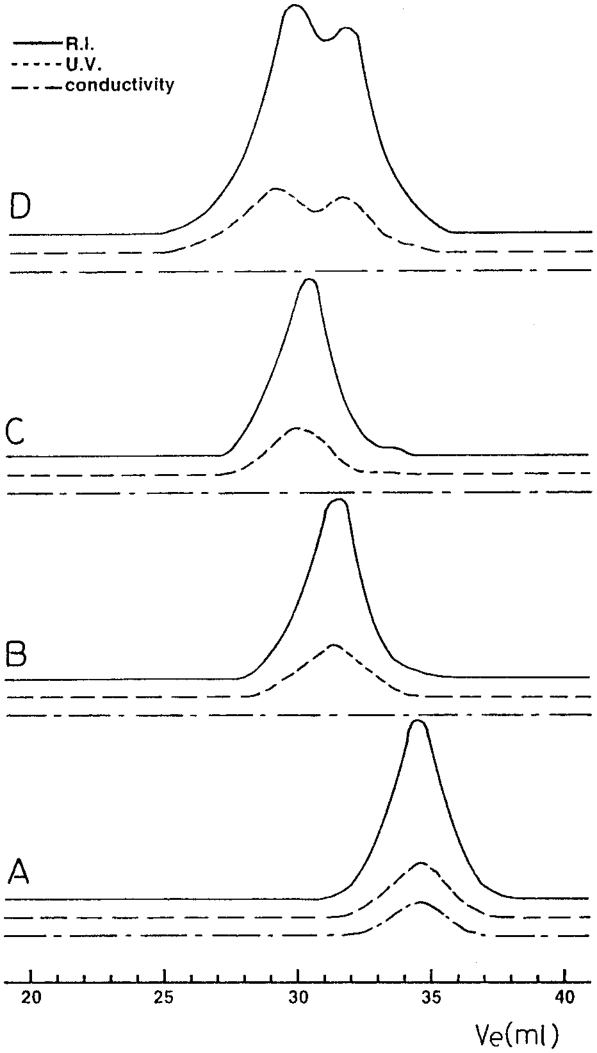

Figure 2. GPC traces of **1** (A), and of the coupling products with a di- (B), tri- (C), and tetracarboxylate (D). (Samples, runs 1–3 in Table 1; column, TSK-G3000HXL + TSK-G4000HXL; eluent, THF, 1 mL/min.)

Although the heat treatment at 100 °C was sufficient for the monofunctional benzoate anion to cause the quantitative ring-opening reaction of the pyrrolidinium salt,[19] the ring-opening reaction for the ion-exchange

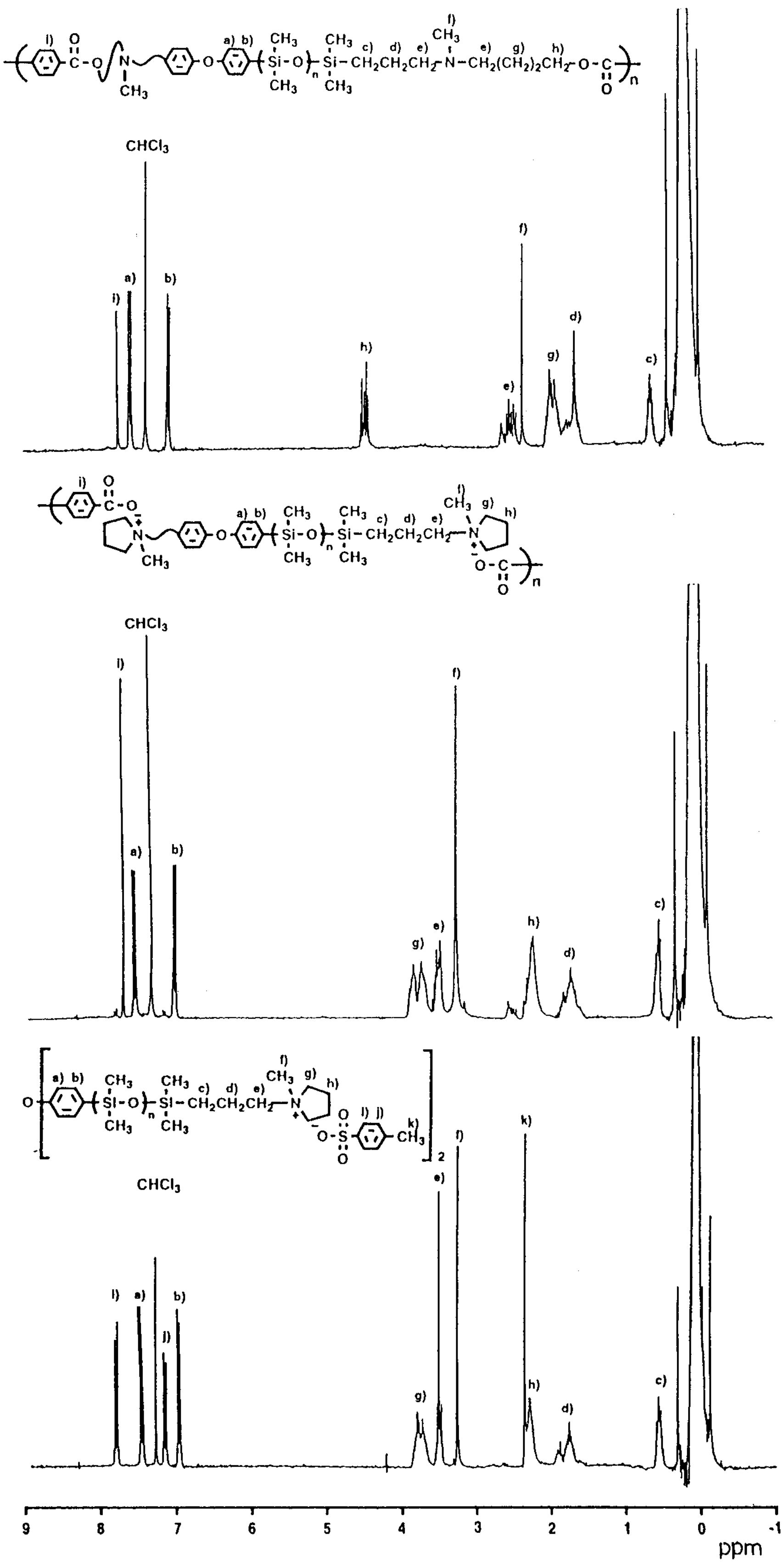

Figure 3. 270 MHz ^{1}H-NMR spectra of **1′** (bottom) and the coupling product with a dicarboxylate before (middle) and after (top) the heat treatment at 120 °C. (Sample: run 4 in Table 1, CDCl$_3$, 40 °C.)

products of **1** and **1′** with plurifunctional carboxylates required the higher temperature of 120 °C.

^{1}H-NMR spectral analysis of the product after the heat treatment at 120 °C (Figure 1, top) showed an quantitative ring-opening reaction to occur. Thus the signals due to pyrrolidinium salt groups at 3−4 ppm are replaced by those due to the amino−ester groups at 4.37 ppm (ester methylene protons as a triplet) as

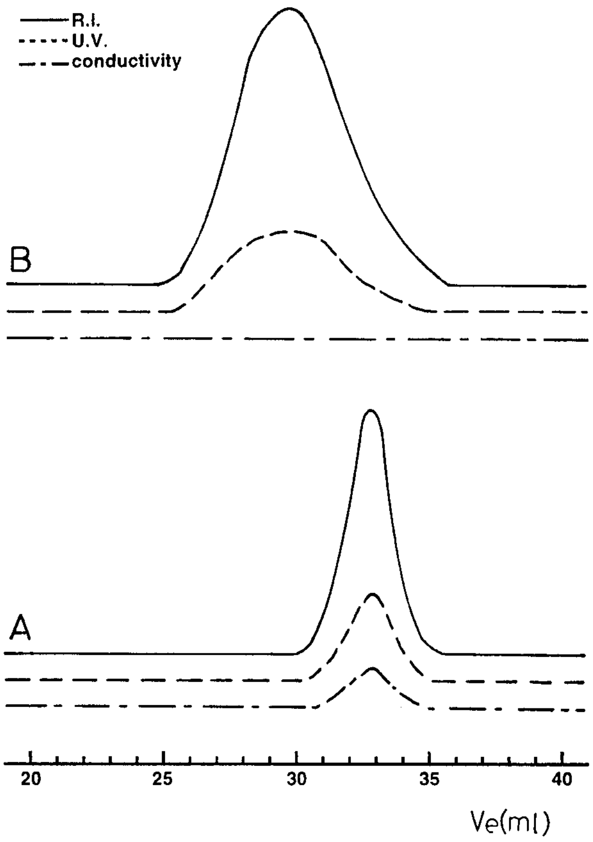

Figure 4. GPC traces of **1′** (A) and the coupling product with a dicarboxylate. (Sample, run 4 in Table 1; column, TSK-G3000HXL + TSK-G4000HXL; eluent, THF, 1 mL/min.)

well as 2.26 and 2.42 ppm (*N*-methyl and *N*-methylene protons, respectively). The ring-opening reaction was also evidenced by IR spectroscopic analysis (not shown) by the appearance of the ester absorption at 1730 cm^{-1} after the heat treatment.

GPC results on the ion-exchange and subsequent covalent fixation products between **1** and a series of plurifunctional carboxylates are collected in Figure 2. The chromatograms for the reaction products between **1** and either bi- or trifunctional carboxylates are unimodal, and the molecular weights of the products are estimated to be nearly two and three times of that of the starting **1**, respectively. The conductivity response is completely eliminated after the heat treatment, indicating that the ionic groups are no longer present. This is consistent with the complete covalent conversion of ionic groups through the nucleophilic attack of carboxylate anion toward the pyrrolidinium ring. On the other hand, the coupling product of **1** with tetracarboxylate no longer shows a unimodal distribution. This is consistent with the less efficient conversion in the ion-exchange reaction with this carboxylate (Table 1).

The ion-exchange and covalent fixation reactions with the bifunctional prepolymer, **1′**, was then carried out with a series of plurifunctional carboxylates. With a bifunctional carboxylate, a linear, chain-extended product, namely a "segmented" poly(DMS), was obtained as confirmed by ^{1}H-NMR spectroscopic (Figure 3) and GPC chromatographic (Figure 4) analyses. As in the case of the monofunctional counterpart, **1**, an efficient anion-exchange reaction and a subsequent ring-opening reaction took place to produce a product of substantially higher molecular weight than that of the starting **1′**. The molecular weight polydispersity for the obtained "segmented" poly(DMS) was higher as a consequence of the polycondensation reaction.

Finally, the ion-exchange and covalent fixation reactions of **1′** with tri- and tetrafunctional carboxylates were carried out. The ion-exchange reaction resulted in pseudo-network products, in which poly(DMS) segments are connected through Coulombic interaction. The pseudo-network products were found to remain soluble in a good solvent like THF. This is presumably because the attractive force between ionic groups is insufficient to fix polymer segments permanently by overcoming the thermal perturbation of macromolecules in solution. The detailed solution property of the pseudo-network is beyond the scope of the present paper but will be a subject of further investigation. This unique solution property of pseudo-network products allows one to examine these products by means of solution ^{1}H-NMR spectroscopy. In Figure 5, the spectra of the ion-exchange products of **1′** with tri- and tetrafunctional carboxylates are listed. The nearly quantitative ion-exchange reaction was confirmed to occur in both reactions. This is in contrast to the case of the monofunctional counterpart, **1**, giving only a 65% ion-exchange yield with a tetrafunctional carboxylate under similar reaction conditions.

The subsequent heat treatment of ionically-linked, pseudo-network products at 120 °C could convert the ionic bond to the covalent one to produce permanent gel products. They were no longer soluble but only swollen in a good solvent like THF. The ring-opening reaction occurring as a result of the heat treatment was evidenced by the IR spectroscopic analysis shown in Figure 6. The absorption at 1730 cm^{-1} due to the ester groups appears after the heating, and that at 1580 cm^{-1} due to carboxylate salt groups is eliminated without any noticeable change in other spectral regions. The network products obtained in the present system are considered as a "model network", in which both the number of the segment at the junction points and the length of the segments between the junction points are precisely defined.[18,22–24]

In conventional cross-linking processes, however, a stepwise reaction continues to produce junction points (and eventually cross-linking points) until the reaction system reaches a gel point. For example, the gel point from bi- and a trifunctional reagents, and that from bi- and a tetrafunctional ones are reached at 75 and 58% conversions, respectively.[25] At this stage, the reaction medium loses fluidity even though unreacted functional groups are still present along or at the chain end of the segment. The further reaction of remaining groups is inevitably retarded due to the increasing difficulty of diffusion of polymer segments in the gel matrix. In consequence, the concurrence of structural defects in network structures, such as free branches and the lack of uniformity in branch numbers at the junction point, would be inevitable even as the gel content is observed to be quantitative. The present ion coupling process, on the contrary, can provide a unique means to overcome the gel point limitation to produce network polymers of predetermined architectures through the prefixation of macromolecules by the ionic interaction and the subsequent covalent fixation process.

The results on the ion-exchange and covalent fixation reactions between **1**, **1′**, and a series of plurifunctional carboxylates are summarized in Table 1. The recovered yields after the precipitation treatment are nearly quantitative in each coupling reaction, and the efficient

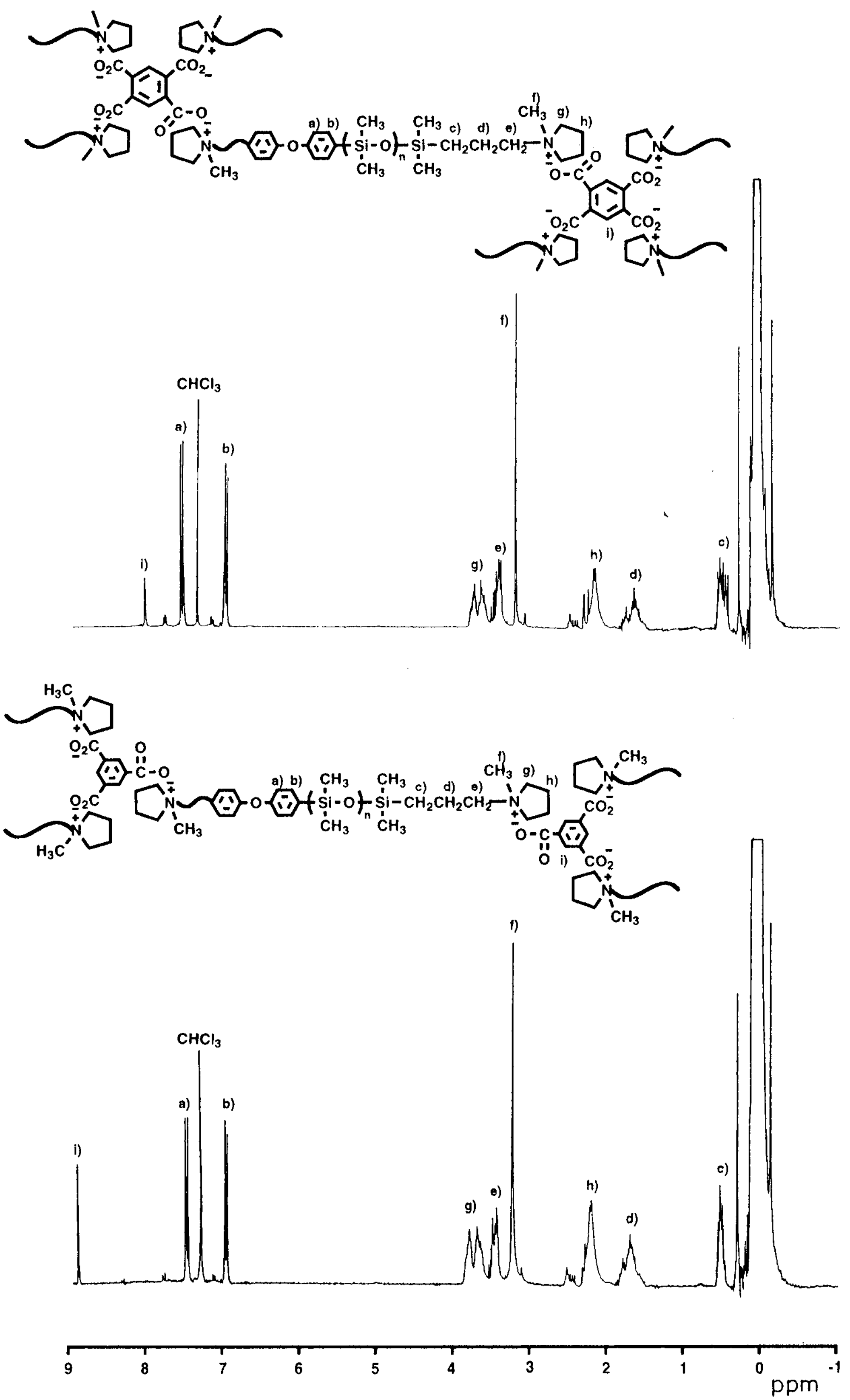

Figure 5. 270 MHz ^{1}H-NMR spectra of the coupling products of **1′** with a tri- (bottom) and a tetracarboxylate (top). (Samples: runs 5 and 6 in Table 1, $CDCl_3$, 40 °C.)

ion-exchange reaction was observed in the reactions of **1** with bi- and trifunctional carboxylates and of **1′** even with tetrafunctional ones. Consequently, this unique ion-exchange process can lead to the formation of the relevant branched (star), “segmented”, and cross-linked (model network) poly(DMS) structures.

The swelling degrees of the obtained poly(DMS) networks were measured and are listed in the last column of Table 1. The swelling degree is higher when the molecular weight of the prepolymer, **1′**, is higher, and is lower when the number of the segment at the junction point is increased from 3 to 4 by the choice of

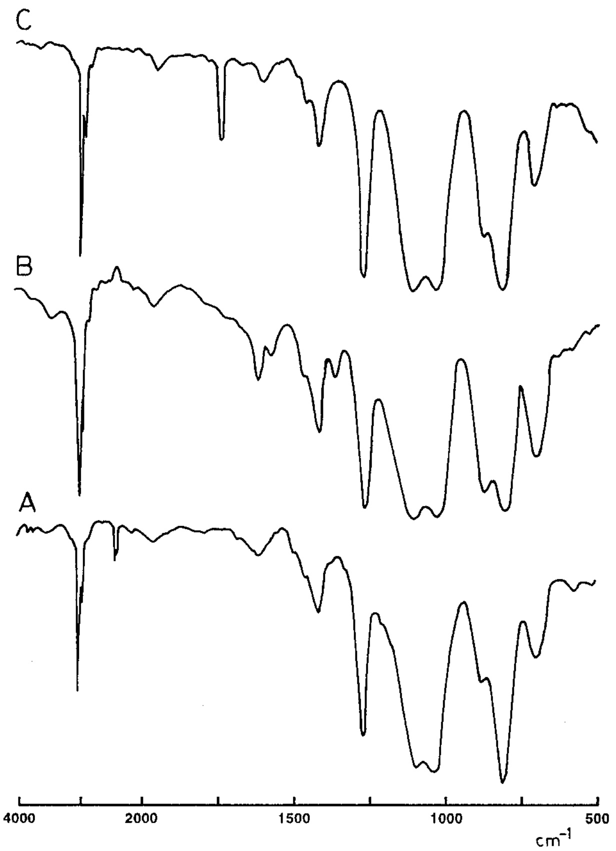

Figure 6. FT-IR spectra of **1**′ (A) and the coupling product with a tetracarboxylate before (B) and after (C) the heat treatment at 120 °C. (Sample: run 6 in Table 1.)

the carboxylate functionalities. This swelling order accords with the cross-linking density estimated from the molecular weight of **1**′ and from the number of functionalities of plurifunctional carboxylates. This is indicative of the modulation of the cross-linking density by the present process with **1**′.

In conclusion, a novel self-assembly process has been developed by making use of Coulombic interaction between hydrophobic macromolecules bearing cyclic onium salt groups at their chain ends and plurifunctional carboxylates. The ion-exchange reaction takes place efficiently at a hydrophobic polymer/aqueous interface. The subsequent covalent fixation of ionically-combined, self-assembled structures has been achieved by a simple heat treatment, where the ring-opening reaction of cyclic onium salt groups takes place selectively as a result of a nucleophilic attack of a carboxylate counteranion.

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