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Tailored synthesis and swelling control of polystyrene/poly(THF) two-component polymer networks

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A series of two-component polymer networks consisting of poly(tetrahydrofuran) [poly(THF)] and polystyrene segments (**3**) was produced through a macromolecular ion-coupling reaction between telechelic poly(THF) having pyrrolidinium salt groups (**1**) of various molecular weights, and a series of poly(styrene-*co*-tetrabutylammonium acrylate) (**2**) having carboxylate contents of up to *ca.* 20 mol%. The coupling reaction proceeded efficiently by simple coprecipitation of a THF solution of an equivalent mixture of **1** and **2** into cold water to combine the two prepolymers by Coulombic interaction. The subsequent heat treatment of the ionically linked pseudo-network product led to covalently linked, permanent network polymers consisting of the two different segment components. The equilibrium swelling degree of a series of network copolymers in toluene was found to be controllable either by the molecular weight of **1** or by the carboxylate content of **2**. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Although extensive crosslinking process have been developed to form macromolecular network structures, still few systems provide an efficient means to give a 'model network' with control of the principal structural parameters, such as the precise chemical structure and the exact position of the junction points, and the number of branches at the junction point as well as the branch segment length between them[1]. Hence, a novel crosslinking reaction process to provide a well-defined network structure is of particular importance to realize optimal performance not only in conventional network polymer materials, such as resins, rubbers and coatings, but also in intelligent polymer network devices having stimuli-responsive, mechanochemical and release-control functions[2–5].

We have recently proposed a new polymer–polymer reaction system[6–8] in which the ion-coupling reaction of telechelics having a series of cyclic onium salt groups is utilized to synthesize graft and network copolymers consisting of poly(tetrahydrofuran) [poly(THF)] and polystyrene segments. This particular macromolecular coupling process is unique in combining immiscible polymer segments first by Coulombic attraction force, followed by the permanent fixation of the two segments through conversion of the ionic linkages to covalent linkages. We have also described the unique swelling behaviour of thus produced two-component network copolymers in solvent mixtures with contrasting solubility properties towards the two different segments[9–11].

As an extension of the preceding studies, we report in the present paper on the synthesis of polystyrene/poly(THF) copolymer networks having a wide range of crosslinking densities. Precise control of the swelling degree of these network copolymers has been achieved through variation of the structural parameters of the prepolymers involved in the coupling reaction.

EXPERIMENTAL

Materials

Poly(THF) having pyrrolidinium salt end groups (**1**). A series of bifunctional poly(THF)s having pyrrolidinium salt end groups was synthesized according to the reported procedure[12] in which bifunctional living poly(THF), prepared with trifluoromethanesulfonic anhydride (triflic anhydride) as initiator, was subsequently reacted with an excess amount of 1-methylpyrrolidine.

Polystyrene having pyrrolidinium salt end groups. The synthesis of a bifunctional polystyrene having pyrrolidinium salt end groups was detailed elsewhere[13], where a bifunctional living polystyrene prepared with sodium naphthalene was treated with a chlorosilane derivative having a protected hydroxyl group [$ClSi(CH_3)_2(CH_2)_3O$-$Si(CH_3)_3$]. The subsequent deprotection, followed by tosylation and finally quaternization with 1-methylpyrrolidine, allowed us to produce telechelic polystyrene having pyrrolidinium salt end groups. The molecular weight of the telechelic polystyrene used in the present study was 6200.

*Poly(styrene-*co*-tetrabutylammonium acrylate) (2).* A series of poly(styrene-*co*-tetrabutylammonium acrylate)s having different acrylate contents was prepared by the

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Table 1 Coupling reaction between telechelic poly(THF) having pyrrolidinium salt groups (**1**) and poly(styrene-*co*-tetrabutylammonium acrylate) (**2**)[a]

Run	**1**	**2**		Recovered yield (%)	Gel content (%)[b]	Segment ratio (DP/DP)[c]
	$M_n \times 10^{-3}$ (g.p.c.)	$M_n \times 10^{-3}$ (g.p.c.)	Carboxylate content (mol%)			
1	2.3	31	1.4	92	88 (80)	32/72
2	2.3	37	3.6	93	89	32/28
3	2.3	46	9.8	95	86	32/10
4	2.3	110	18.2	94	85	32/4.4
5	2.3	120	22.5	91	84	32/4.4
6	4.0	42	6.8	91	88 (77)	56/15
7	4.0	46	9.8	94	87 (80)	56/10
8	4.0	81	14.0	94	83 (77)	56/4.0
9	4.0	110	18.2	96	84 (78)	56/5.5
10	5.8	31	1.4	88	88 (80)	81/72
11	5.8	46	9.8	96	88 (75)	81/10
12	5.8	81	14.0	94	85 (80)	81/4.0
13	5.8	110	18.2	96	84 (80)	81/5.5
14	5.8	120	22.5	95	85 (74)	81/4.4
15	7.0	37	3.6	91	94	97/28
16	7.0	81	14.0	86	93	97/4.0
17	7.0	110	18.2	96	85	97/5.5
18	7.0	120	22.5	92	90	97/4.4

[a] The equimolar mixture of **1** and **2** with respect to ionic groups (*ca.* 0.2 g) in THF (*ca.* 10 wt/vol%) was precipitated three times into water (500 ml) below 5°C and stirred for 2 h

[b] By heat treatment at 110°C for 24 h. Values in parenthesis are those after the first precipitation

[c] Segment length between the junction points in the network polymer

neutralization of poly(styrene-*co*-acrylic acid) with tetrabutylammonium hydroxide. Thus a weighed amount (*ca.* 1.5 g) of poly(styrene-*co*-acrylic acid) was dissolved in 20 ml dioxane and mixed with an equivalent amount of tetrabutylammonium hydroxide (in methanol, 1 M, from Nacalai Tesque) under N_2. The homogeneous mixture was stirred for 24 h at ambient temperature, subjected to freeze drying *in vacuo* and finally dried at 50°C for 24 h. The yield of the product was quantitative and the complete neutralization of carboxylic acid groups was confirmed by i.r. spectroscopic analysis. Samples of **2**, derived from poly(styrene-*co*-acrylic acid) having molecular weight of $31-120 \times 10^3$ and polydispersity index of *ca.* 1.5, were used in the present study as listed in *Table 1*.

Procedures

Ion-coupling reaction of **1** and **2**. A mixture of **1** and **2** (*ca.* 0.2 g) with an equimolar quantity of ionic groups was dissolved in THF (*ca.* 10 wt/vol%), and added dropwise slowly into 500 ml of ice-cooled, deionized water below 5°C under vigorous stirring. The stirring was continued for 2 h, and the precipitated product was recovered by filtration and subjected to up to three repeated precipitation treatments following an identical procedure. The recovered product was then dried *in vacuo*. The heat treatment was performed for a sample film cast from chloroform on a Teflon plate in a vacuum desiccator thermostated at 110°C for 24 h. The gel product thus produced was subjected to a Soxhlet extraction with THF for 24 h. The ion-coupling reaction between the relevant telechelic polystyrene and **2** was performed similarly, but through precipitation into methanol[13].

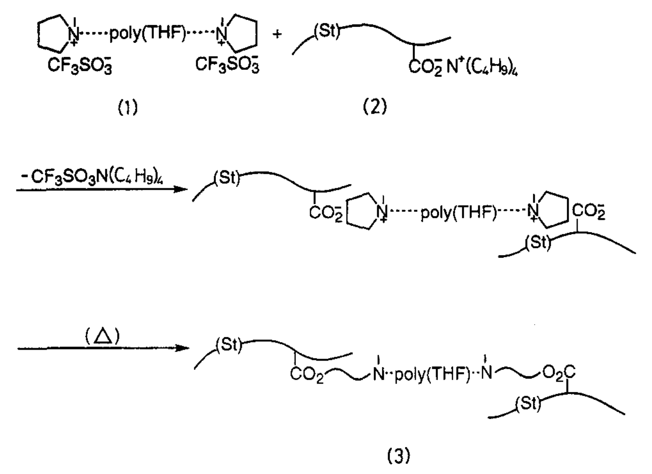
Measurements

Fourier transform infra-red (*FT*i.r.) spectra (40 scans) were taken with a Shimadzu model FTIR 8100 infra-red spectrophotometer on samples cast on NaCl plates. The degree of swelling (by weight) for a series of network products was determined by measuring the weight of the dry network and of the swollen network samples after immersion in toluene at ambient temperature for 24 h.

RESULTS AND DISCUSSION

In conventional crosslinking processes, a stepwise reaction continues to produce junction points (and eventually crosslinking points) until the reaction system reaches a gel point. For instance, the gel-point conversion for a bi- and a trifunctional reagent is calculated to be 71%, and that for a bi- and a tetrafunctional one to be 58%[14]. At the gel point, the fluidity of the medium is lost even though unreacted functional groups are still present. Further reaction is thus inevitably retarded owing to the difficulty of diffusion of polymer segments in the gel matrix. As a consequence, structural defects in the network, such as free branches and lack of uniformity in the number of branches at the junction point, may not be excluded even when the observed gel content is nearly quantitative[1,15–17].

The present ion-coupling process (*Scheme 1*), on the other hand, can provide an alternative means to produce a copolymer network of predetermined architecture through ionic self-assembly and subsequent covalent conversion processes. Moreover, this system can offer a unique opportunity to overcome the gel-point limitation in the conventional, stepwise crosslinking processes. Thus the reaction between telechelic poly(THF) having pyrrolidinium salt groups (**1**) and poly(styrene-*co*-tetrabutylammonium acrylate) (**2**) was performed. The respective reaction between telechelic polystyrene having pyrrolidinium salt groups and **2** was also carried out for comparison purposes[13]. The five-membered cyclic ammonium salt groups at the end of these telechelic polymers can undergo



Scheme 1

a selective ring-opening reaction by nucleophilic attack of a carboxylate counter anion at elevated temperature[12]. The carboxylate-containing prepolymer, **2**, was prepared by the treatment of poly(styrene-*co*-acrylic acid) with an equivalent amount of tetrabutylammonium hydroxide, and was found to be soluble in THF for a wide range of carboxylate content of up to *ca.* 20 mol%. This is in contrast to the corresponding copolymer containing sodium acrylate groups, which is insoluble in THF when the carboxylate content is greater than *ca.* 5 mol%[6].

The coprecipitation between a series of **1** and **2** was carried out simply into cold water with a THF solution of both prepolymers. This coprecipitation was repeated up to three times with a high recovery yield. The recovered, ionically linked products remained soluble in THF regardless of the molecular weight of **1** and the carboxylate content in **2**. The subsequent heat treatment then produced products that were no longer soluble but were swollen in THF and other common solvents. This soluble nature of ionically linked networks allows us to perform a repeated coprecipitation procedure to achieve a high ion-exchange yield in the coupling reaction between the prepolymers. Hence, this process provides a unique means to combine different polymer segments at the specific reactive sites to cause the eventual ring-opening (crosslinking) reaction.

The i.r. spectra of the products before and after the heat treatment (*Figure 1*) show that the absorption of ester groups at 1740 cm^{-1} appears after the heat treatment at 110°C for 24 h, along with almost complete removal of the absorption of carboxylate salt groups at 1600 cm^{-1} without further noticeable change in the spectrum. This result confirms high efficiency in the ion-exchange reaction, taking into account also the high recovery yield in the coprecipitation treatment between **1** and **2**.

The series of gel products thus obtained was subsequently subjected to extraction with THF. As summarized in *Table 1*, the gel content was observed to reach as high as 90% by repetition of the coprecipitation in any combination of **1** and **2**. Thus the repeated coprecipitation apparently promoted the ionic combination of prepolymers by expelling water-soluble salt (tetrabutylammonium triflate) into the aqueous phase. The minor sol fraction was analysed and found to comprise uncoupled poly(THF) prepolymer.

The swelling behaviour of poly(THF)/polystyrene networks possessing different network parameters, i.e. segment ratios in *Table 1*, was then examined in toluene, a good solvent for both polymer components. In addition, a polystyrene network was studied for comparison purposes. The results are summarized in *Figure 2*.

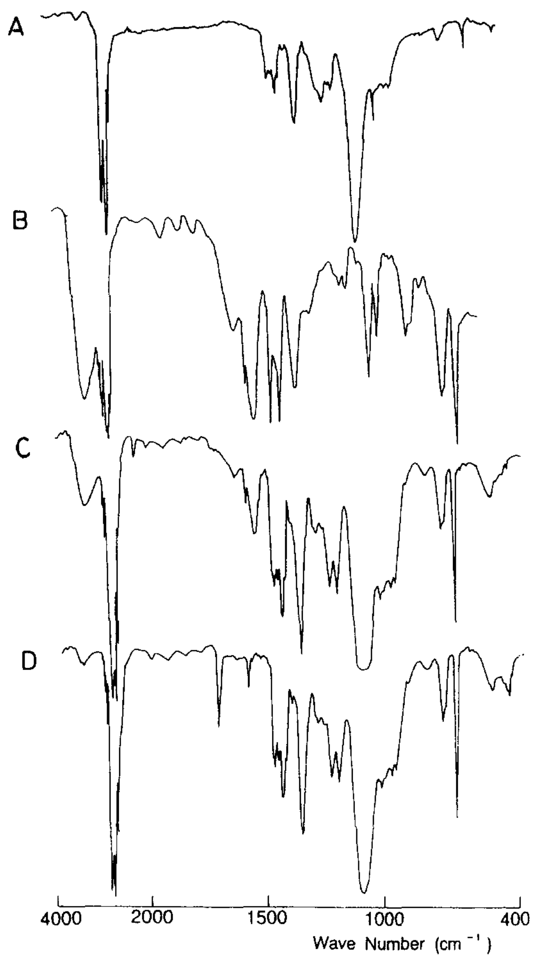


Figure 1 I.r. spectra of poly(THF) having pyrrolidinium salt end groups (A), poly(styrene-*co*-tetrabutylammonium acrylate) (B), and the coupling product before (C) and after (D) the heat treatment at 110°C (run 6 in *Table 1*)

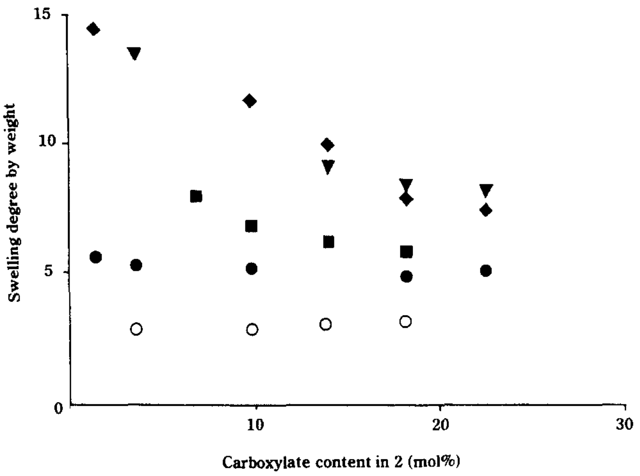


Figure 2 The swelling degrees of poly(THF)/polystyrene networks having different segment ratios [molecular weight of poly(THF): 2300 (●), 4000 (■), 5800 (◆) and 7000 (▼)] and (O) those of polystyrene networks (molecular weight of the telechelic polystyrene: 6200)

The swelling degree of network copolymers (**3**) obtained after three precipitation treatments, in which the ion-coupling reaction between **1** and **2** was almost quantitative, showed a linear correlation with the carboxylate content in **2**. By contrast, the swelling degree of **3** obtained after the first precipitation failed to show such correlation with the carboxylate content in **2**. This is in accordance with an insufficient ion coupling between prepolymers **1** and **2** after the first precipitation. The gel content after the first precipitation was lower than those after the repeated (three times) precipitation (*Table 1*). An increase in the carboxylate content in **2** corresponds to a decrease in the average polystyrene chain length between carboxylate groups, i.e. the crosslinking points, leading to the increase of crosslinking density. Hence, the observed good correlation between the swelling degree and the carboxylate content in **2** in a series of network copolymer systems is an indication of efficient coupling of reactive groups located both in **1** and **2** in the present process.

The increment in the slope for the relationship between the swelling degree and the carboxylate content in **2** was obviously higher for the gel from **1** of the higher molecular weight. This is presumably due to the repulsive interaction between the immiscible poly(THF) and polystyrene segments in the network, causing further network expansion during the swelling process in toluene. Thus the swelling degree of the polystyrene network was less influenced upon variation of the network size (*Figure 2*). Nevertheless, the hydodynamic volume of polystyrene itself is smaller than that of poly(THF) of identical molecular weight, and this could also cause the decrease in the swelling degree of the homopolymer network in comparison with the copolymer network, **3**.

In conclusion, the present macromolecular ion-coupling process, which makes use of the unique reactivity of telechelic polymers having cyclic onium salt groups, can provide a simple and efficient means to prepare networks with controlled structures with respect to the average segment length between junction points. Variation of the swelling degree of the gel products is achieved by the predetermined structural parameters of the prepolymers.

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