Synthesis of Macromolecular Networks via Coupling of Star-shaped Polymers

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ABSTRACT

In the present work, the two-step so-called "in-in" method, is used to produce model networks with well-defined and controllable structure. For this purpose, two different networks are produced: (a) polystyrene network, including polystyrene star-shaped polymers connected by linear polystyrene chains. (b) polystyrene-polyisoprene network, including polystyrene star-shaped polymers connected by linear polyisoprene chains. The structural parameters of the synthesized networks are determined by SEC, light scattering and theoretical calculations later. In such anionically synthesized networks, each junction point, carries many pendent chains on itself (the arms of the initial star polymer), which have rotational degrees of freedom under the conditions of use.

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Key Words:
macromolecular network;
star-shaped polymer;
bifunctional chain;
active site;
pendent chains.

INTRODUCTION

The history of polymer materials shows that the usage and technology of polymer networks were well established prior to knowledge of their molecular structure and scientific understanding of their properties [1]. In order to investigate the property-structure relationship of polymer networks, it is useful to synthesize model networks with well-defined and controllable structure. These model networks are usually obtained by reacting the active chain ends of anionically synthesized

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bifunctional polymers with an appropriate bis-unsaturated monomer like divinyl benzene (DVB). Lutz et al. considered to extend this method by using multifunctional star-shaped polymers instead of bifunctional linear ones. These researchers have adopted two approaches in this way[2]: in one approach the living star-shaped polymer (with the active sites at the end of its arms) is reacted with a stoichiometric amount of DVB as a coupling agent, and in the second approach the living star-shaped polymer is functionalized first with hydroxyl groups (through the reaction with ethylene oxide), then these hydroxyl terminated star-shaped molecules are reacted with appropriate di- or tri- isocyanate compounds. The result of this investigation is not published yet.

Up to the present day, there have been different methods for the synthesis of star-shaped polymers via anionic polymerization, including "deactivation method"[3-6], which is one aspect of the more general "arm-first method"[7-9], "core-first method"[7,10-12], "in-out method"[9,13-19] and the new "in-in method" which has recently been presented by the authors of this paper [20,21].

The basis of the two-step "in-in" method is generated from the fact that star polymers with polydivinyl benzene core, synthesized by the arm-first method, include many un-reacted double bonds in their core[9,11,6]. These double bonds can be attacked by the carbanions of some monomers such as styrene or dienes.

In the present work, the two-step so-called "in-in" method is used to produce model networks with well-defined and controllable structure. For this purpose, two different networks are produced: (a) PS network, including polystyrene star-shaped polymers connected by linear polystyrene chains together and, (b) PS/PI network, including polystyrene star-shaped polymers connected by linear polyisoprene chains. After synthesis of these networks, attempts are made to characterize and specify their structure.

EXPERIMENTAL

Materials

Tetrahydrofuran (Merck, molecular weight 72.11, 99% pure) was distilled over sodium wire. The blue colour of THF included sodium wire and a small amount of benzophenone was an indicator for the lack of the protonic impurities. Styrene (Merck, molecular weight 104.15) and divinyl benzene (Merck, molecular weight 130.1, contained roughly 65% of DVB and 33% ethylvinylbenzene) were distilled twice under vacuum, over sodium wire. Isoprene (Merck, molecular weight 68.12) was distilled twice in atmospheric pressure, over sodium wire. n-Butyl lithium (Merck, molecular weight 64.06, solution 15% in n-hexane) was used as monofunctional initiator and sodium naphthalene synthesized from the reaction of sodium with naphthalene in THF solution under Argon pressure [22], was used as bifunctional initiator. The molarity of both initiators were determined by titration with acetanilide (Merck, molecular weight 135.17, 99% pure). The use of diphenyl methane for the titration of butyl lithium is necessary as well.

Apparatus

The reaction was carried out in a one-liter reactor, fitted with magnetic stirrer, pure argon inlet, temperature control, burettes containing the solvent and monomers to be added, and a sampling device. The apparatus was designed to operate under a slight argon overpressure, allowing all the reaction steps to be carried out under exclusion of air and moisture.

The Experiments Performed in Two Steps

(1) Synthesis of PS Star-shaped Polymer Adopting Arm-first Method

The experiment was run in tetrahydrofuran (THF) solution at -30°C. n-Butyl lithium (n-BuLi) was the initiator for the synthesis of living polystyrene chains. A fraction of living polystyrene solution was sampled out for purpose of characterization. Then divinyl benzene (DVB), three times diluted in distilled THF, was added at once to the system with efficient stirring. The mole ratio of DVB to BuLi was about 10. The polymerization of DVB was conducted under the same conditions as that of styrene. The star polymer was precipitated, dried and characterized by SEC (size exclusion chromatography) and light scattering techniques.

(2) Synthesis of Macromolecular Network

First, bifunctional linear living polystyrene or polyisoprene chains were synthesized with anionic polymer-

ization in THF solvent with sodium naphthalene as the initiator. A fraction of solution was then sampled out for characterization. Then 4 g of star polymer, synthesized and characterized in the previous step was dissolved in THF and added to the system. The system was efficiently stirred for a few seconds and then the stirrer was turned off. After a while, gelation occurred in the system, so that the magnet was not able to stir the product. The system was kept alone for 1 h, then the active sites of the network were killed with methanol and the final product was dried. In order to measure the gel content of the product, soxhlet extraction was done on the samples with THF for at least 4 h.

Measuring Instruments

Light scattering measurements were carried out on a SEMATech apparatus using laser light with $\lambda = 632.8$ nm in toluene solution. SEC Measurements were carried out on a Waters apparatus fitted with ultra styrogel columns (10^3 Å- 10^4 Å - 10^5 Å - 10^6 Å). The elution solvent was THF, with the flow rate of 1.5 mL/min.

RESULTS AND DISCUSSION

In the present work, the new so-called "in-in" method was used for the synthesis of macromolecular networks. In order to have more information about this new method, the authors of this paper, refer the readers to their previous papers[20, 21]. However, it should be explained briefly that this method includes two different steps. In the first step, polystyrene star-shaped polymer with polydivinyl benzene core is synthesized as the same way as an arm-first method. The product is precipitated, dried and well characterized. In the second step, first, living polystyrene (or polydienes) chains are synthesized via anionic polymerization. Then a known amount of the star polymer, synthesized in the previous step, is dissolved in THF and added to the system. The carbanions located at the end of the living chains, attack the double bonds existing in the core of the star molecules and attach to them by opening these bonds. This method is successfully used for the synthesis of PS double star polymer[20] and PS/PI hetero-arm star polymer[21].

In this research work, the same method was adopted, just in the second step, a bifunctional initiator (sodium naphthalene) was used instead of monofunctional ones. Therefore, in the second step of this process, linear bifunctional polystyrene (or polydiene) chains were produced initially. Then a known amount of the star polymer synthesized and well characterized in the first step, was dissolved in THF and added to the system. It was expected that each end of these bifunctional chains, attach to the cores of different star polymers and produce a macromolecular network (Figure 1).

In order to confirm the above expectation, two different experiments were carried out: in the first step of both experiments, PS star-shaped polymer was synthesized by an arm-first method, in THF solution with n-butyl lithium as the initiator. The product was precipitated, dried in an oven with 50°C for at least 12 h and well characterized by SEC, light scattering and viscometry techniques.

The second step of the foregoing method was done with bifunctional PS and bifunctional PI chains in exp. 1 and exp. 2, respectively. In both experiments, after anionically polymerizing of bifunctional chains (in THF solution and with sodium naphthalene as the initiator), 4 g of PS star-shaped polymer, synthesized in the first step, was dissolved in THF and added to the system. The system was thoroughly stirred and then the stirrer was turned off. In both experiments after some minutes, gelation occurred in the system, so that the magnet was not able to stir the product.This phenomenon confirms the explained mechanism in Figure 1. It should be said that in exp. 2, where bifunctional PI chains were used, the rate of gel formation was lower than exp. 1. It is because the reaction of isoprenyl carbanions with the double bonds, existing in the core of the star polymer, is slower than styryl carbanions. Therefore, in the case of using bifunctional isoprene chains, the addition of a small amount of styrene monomer to the system, prior to introducing the solution of star polymer, would change the isoprenyl lithium end chains to styryl lithium ones and increases the rate of gel formation.

In order to characterize and specify the structure of the synthesized networks, first of all SEC and light scattering measurements were done on the samples. The results are shown in Table 1. It should be mentioned that although SEC is well suited for determining the molecular weight and polydispersity of the linear precursors, but for the star polymers, SEC technique yields apparent molecular weight, lower than the real

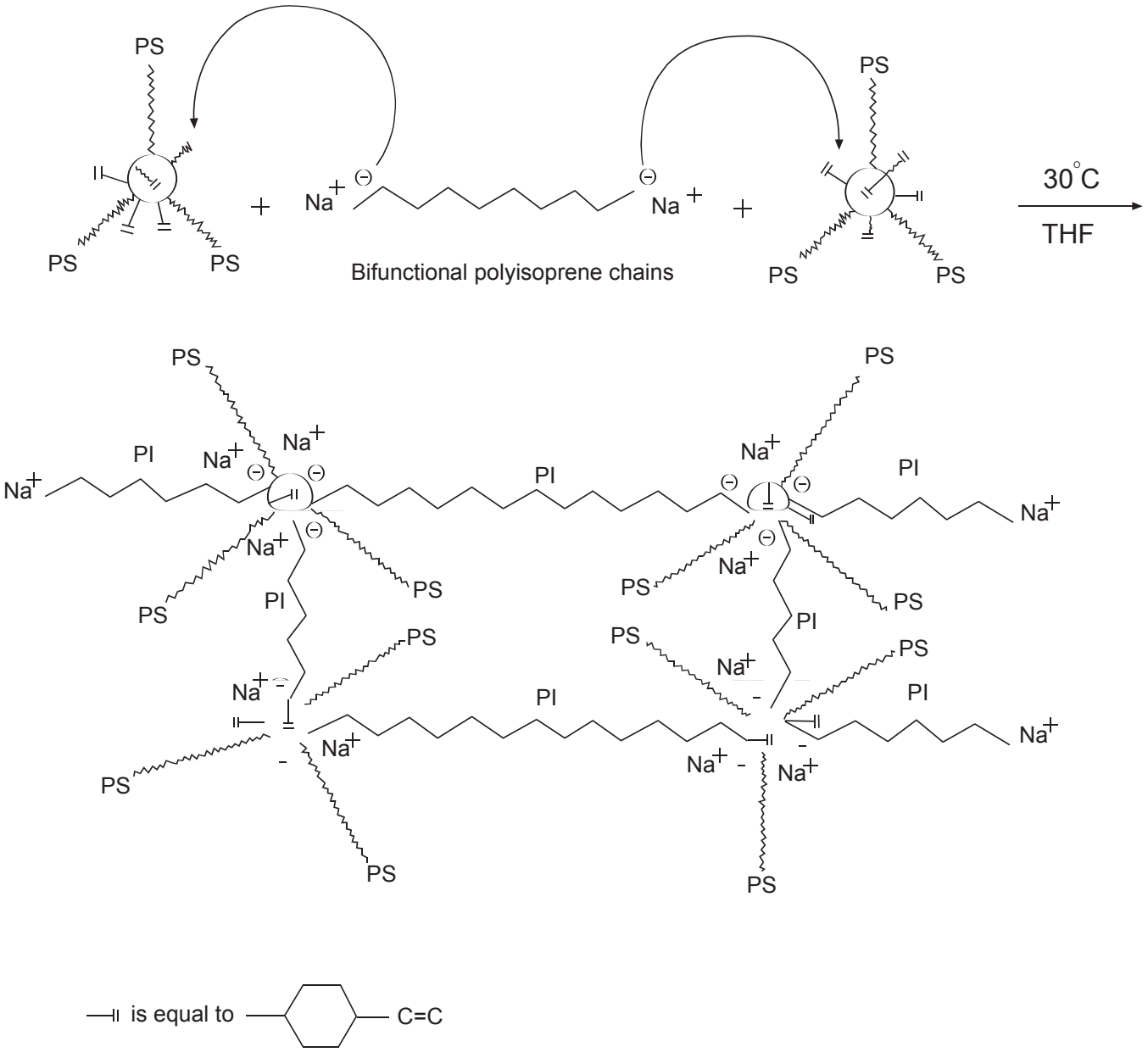

Figure 1. The mechanism of gel formation.

values obtained by light scattering. It is because, the parameter that determines retention in the columns of SEC apparatus, is the hydrodynamic volume of the solute molecules which for the star polymers is much smaller than linear polymers with the same molecular weight[23]. Therefore, the best method for measuring molecular weight of the star molecules is light scattering. However, the SEC trace can quantitatively detect the amount of free precursor in the samples, and gives rough estimate of molecular weight distribution within the star polymers[24].

In addition to the given data in Table 1, the gel content of the synthesized networks was measured as well. For this purpose, first the synthesized gel was dried well. Then the un-reacted chains were separated from the network, in a soxhlet extractor with THF for about 4 h. The weight loss of the well-dried soxhleted sample was measured precisely later. The results are given below:

Gel content for network synthesized in exp. 1 = 97.64%

Gel content for network synthesized in exp. 2 =

Table 1. The measured characteristics of the samples.

Characteristics	PS Arms of the star polymer	Star polymer synthesized in step 1	Bifunctional PS chains	Bifunctional PI chains
$\overline{M}_n$ (SEC),	8,000	---	9,700	24,000
$\overline{M}_W$ (SEC),	12,700	---	13,000	37,000
PDI (SEC)	1.58	1.51	1.34	1.54
$\overline{M}_W$ (LS)	---	267,800	---	---
$\overline{M}_n$ & f (calculated)	* $\overline{M}_n$ = 7,575	**f = 19	*Mn = 10,329	*Mn = 23,860

(*) calculated from the weight of monomer to the moles of initiator; (**) calculated from the following equation [22,30]: $f = M_{star} / [M_{precursor} + (M_{DVB}/Li+)]$.
Molecular weight unit = g/g mol.

92.38%

For both experiments, from the molar concentration of the bifunctional initiator and the volume of the reaction solution, it was possible to calculate the concentration of the active sites presented in the system, prior to addition of the star polymer:

Molar concentration of the active sites in the system for exp. 1 = 8.8×10^{-6} g. mole / mL

Molar concentration of the active sites in the system for exp. 2 = 2.8×10^{-6} g. mole / mL

Then by considering the measured gel content for each experiment, the effective molar concentration of the active sites participating in the network structure ($C_{eff.\ active\ sites}$) was calculated:

$C_{eff.\ active\ sites}$ for exp. 1 = $8.8 \times 10^{-6} \times 0.9764 = 8.592 \times 10^{-6}$ g. mol / mL

$C_{eff.\ active\ sites}$ for exp. 2 = $2.8 \times 10^{-6} \times 0.9238 = 2.586 \times 10^{-6}$ g. mol / mL

The molecular weight of the star polymer, synthesized in the first step and added to the system in the second step for both experiments, has been 267,800 g/g. mole (Table 1). Since 4 g of this star polymer was dissolved in a small amount of THF and added to the reaction system, the molar concentration of the star polymer in the system was calculated as follows (the volume of the reaction solution was about 75 mL):

Molar concentration of the star polymer in the system :

$$\frac{4}{(267{,}800)(75)} = 1.99 \times 10^{-7}$$

It was obvious that in each mL of the reaction solution, in exp. 1 about 8.592×10^{-6} g.mol and in exp. 2 about 2.586×10-6 g.mol of active sites were consumed for connecting 1.99×10^{-6} g.mol of the star molecules. According to the following calculation, the average number of grafting chains on each star molecule for the networks synthesized in exp. 1 and exp. 2 was 43 and 13, respectively:

The average number of grafting chains on each node for exp.1: $8.592 \times 10^{-6} / 1.99 \times 10^{-7} = 43$

The average number of grafting chains on each node for exp.2: $2.586 \times 10^{-6} / 1.99 \times 10^{-7} = 13$

On the basis of the obtained data, the structural parameters of the synthesized networks were specified, which are summarized in Table 2. A schematic view of the synthesized networks is also drawn in Figure 2.

Table 2. The structural parameters of the synthesized networks.

Structural parameter	PS Network (synthesized in exp. 1)	PS/PI Network (synthesized in exp. 2)
Molecular weight of the pendent chains on each node(g/g mol)	8,000	8,000
Average number of the pendent chains on each node	19	19
Molecular weight of the grafting chains between the nodes(g/g mol)	9,700	24,000
Average number of grafting chains on each node	43	13

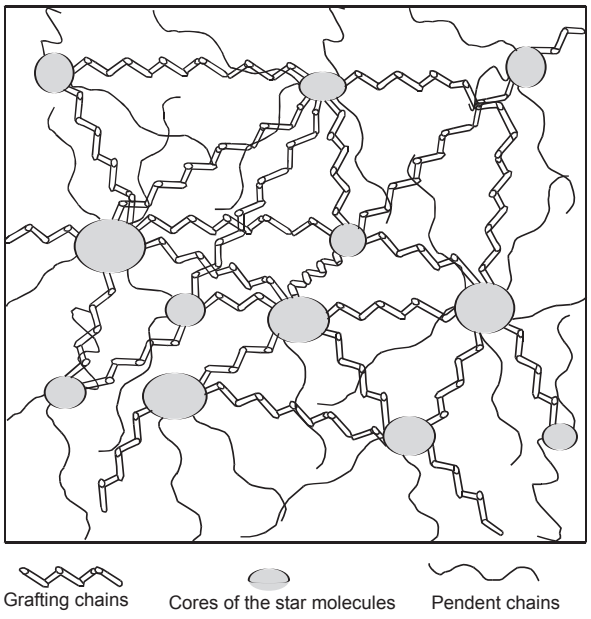

Figure 2. A schematic view of the synthesized network.

CONCLUSION

In this work, the two-step so-called "in-in" method was used for the synthesis of model networks via connecting the star-shaped polymers. It was seen that, in the case of using bifunctional PI chains for connecting the PS star-shaped molecules, the addition of a small amount of styrene monomer to the system, prior to addition of the star polymer, increases the rate of the gel formation.

The structural parameters of the synthesized networks, such as the average length and average number of the pendent or grafting chains on each junction point were determined by SEC, light scattering and theoretical calculations. The molecular weight (or length) of both, pendent and grafting chains on each node is directly dependent on the mole ratio of monomer to the initiator in each step of this process. Moreover, the average number of pendent and grafting chains on each node can be changed to high or low levels by adjusting the mole ratio of (DVB / Li^+) in the first step. Although this is not a quantitative adjustment, but at a constant overall concentration, by increasing the mole ratio of (DVB / Li^+), the number of the arms (pendent chains) and also the size of the cores of the star polymer, synthesized in the first step will be increased. By increasing the size of the cores, the amount of the double bonds remaining inside the cores and consequently the potential of grafting on each node will be increased.

With the use of this method, it is possible to synthesize macromolecular networks with interesting properties. One of the most characteristics of such networks is that, each junction point carries many pendent chains on itself, which can have degrees of freedom under the conditions of use. With the change of the type and length of these pendent chains (for example, using water-soluble polyethylene oxide chains), a wide range of interesting properties in polymeric networks may be achieved.

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