9694 *Macromolecules* **2003,** *36,* 9694−9697

Enantioselective Permeation through Membranes of Chiral Helical Polymers Prepared by Depinanylsilylation of Poly(diphenylacetylene) with a High Content of the Pinanylsilyl Group

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Received October 3, 2003
Revised Manuscript Received November 6, 2003

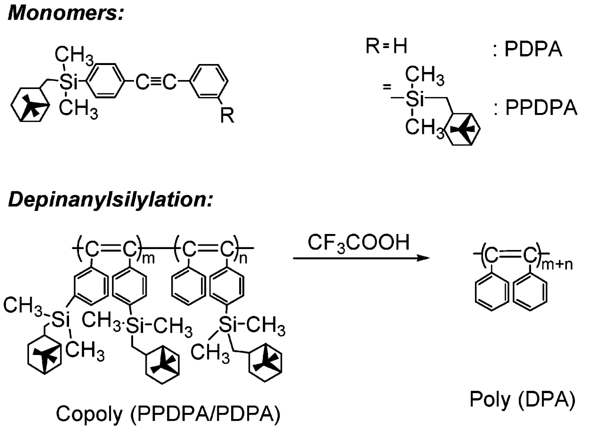
Introduction. Recent vigorous studies regarding polymer synthesis have enabled us to provide polymers with well-defined primary structure.[1] However, generation of specific functions often requires precise management of the secondary structure in addition to control of the primary structure. The most representative example can be seen in proteins whose characteristic second-order structure containing α-helix, β-pleated sheet, etc. plays a very important role in realizing their specific functions. Therefore, appropriate control of the secondary structure makes it possible not only to improve their performances but also to offer various new functions, which is a promising way to highly advanced materials for the future.

The helical structure is the most basic polymer conformation among the secondary structures, and is frequently seen in the functional biopolymer such as DNA, RNA, and enzyme. The helix sense of these biopolymers is generally in one direction, and the helix can be molecularly chiral due to only its second-order structure. Hence, synthesis of chiral helical polymers and their properties and application such as asymmetric reactions and optical resolutions has attracted much attention in recent years.[2−4]

Heretofore, we have investigated the synthesis of substituted polyacetylenes having a chiral helical conformation,[5−7] for example, a poly(phenylacetylene) derivative having two hydroxymethyl groups which was synthesized by asymmetric polymerization using chiral rhodium catalyst, $[Rh(nbd)Cl]_2$−(*R*)-1-phenylethylamine.[6] The formed polymer has a chiral helical structure stabilized by intramolecular hydrogen bonds in solution without any other additives.

Also, chiral dimethyl(10-pinanyl)silyl groups (called as pinanylsilyl groups in this Communication for short) containing poly(diphenylacetylenes) [poly(PDPA)] showed intense Cotton effects[7] in CD spectra due to the chiral helical backbone, and the membrane fabricated from the polymer exhibited excellent enantioselectivity in the permeation of racemic tryptophan.[8] Furthermore, we recently revealed that poly(PDPA) after undergoing complete removal of the pinanylsilyl groups in the membrane state via trifluoroacetic acid treatment (named as "*depinanylsilylation*") maintained the space that was occupied by the pinanylsilyl groups.[9] And quite interestingly the depinanylsilylated membrane retained its chiral helical structure despite the absence of the chiral substituents in the polymer. Such "chiral memory" of the polymer helicity was found first by Yashima's group.[10] This new concept is very interesting, and it is expected that the research fields dealing with the synthesis of chiral helical polymer and their application will become more active.

Scheme 1. Monomer Structures and Depinanylsilylation Method in This Study[a]



m/n = 36/64: poly(**1**)	*de*-poly(**1**)
m/n = 24/76: poly(**2**)	*de*-poly(**2**)
m/n = 0/100: poly(**3**) [poly(PDPA)]	*de*-poly(**3**)

[a] Poly(DPA)s obtained by depinanylsilylation of poly(**1**), poly(**2**), and poly(**3**) are discriminated by attaching the *de*- on the original polymer code.

These findings about poly(PDPA) stimulated us to study the following: (i) enantioselective permeation through membranes having only a one-handed helical conformation as the chiral source; (ii) preparation of porous organic membranes by "*depinanylsilylation*" of the polymers with high content of pinanylsilyl group; (iii) enhancement of permeability due to the molecular-scale voids generated by "*depinanylsilylation*". In this Communication, we report the preparation of chiral porous membranes by "*depinanylsilylation*" of poly(diphenylacetylenes) with high content of the pinanylsilyl group, which are synthesized by copolymerization of 1-phenyl-2-[4-(dimethyl(10-pinanyl)silyl)phenyl]acetylene (PDPA) with 1-[3-(dimethyl(10-pinanyl)silyl)phenyl]-2-[4-(dimethyl(10-pinanyl)silyl)phenyl]acetylene (PPDPA), as shown in Scheme 1. Furthermore, enantioselective permeations through the depinanylsilylated membranes are investigated, and the effect of main chain chirality and the molecular-scale voids on enantioselective permeation is clarified.

Experimental Section. Polymerizations were carried out under dry nitrogen atmosphere by $TaCl_5$-*n*-Bu_4Sn catalyst which is the most powerful one used in the polymerization of diphenylacetylenes.[11] A detailed procedure of polymerization has been described else-

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10.1021/ma035493h CCC: $25.00

Table 1. Copolymerization Results and Enantioselective Permeation of the Original and the Depinanylsilylated Poly(PPDPA/PDPA)[a]

			polymer					permeation of *rac*-tryptophan			
								P ($\times 10^{-12}$ m^2/h)[f]		% ee[g]	
run	code	feed, PPDPA (mol %)	compn,[b] PPDPA (mol % (*m*))	Pi[c] (wt %)	yield (%)	M_w[d] ($\times 10^5$)	$[\alpha]_D^{20}$ (deg)[e]	original	depinanyl-silylated	original	depinanyl-silylated
1	poly(**1**)	40	35.7	59.9	44.7	3.74	+428	5.51	22.5	16.4	10.1
2	poly(**2**)	30	23.8	57.7	48.9	4.21	+876	5.15	19.7	23.1	15.2
3	poly(**3**)[h]	0		52.4	78.9	8.03	+1450	3.60	13.4	54.3	48.5
4[h]								17.6[i]	1450[i]	80.5[i]	58.6[i]

[a] Polymerized in toluene at 110 °C for 4 days, $[M]_{0,\text{total}} = 0.50$ M, $[\text{TaCl}_5] = 40$ mM, $[n\text{-Bu}_4\text{Sn}] = 80$ mM. [b] Estimated by elemental analysis. Here, "*m*" corresponds to the ratio of the PPDPA unit of poly(PPDPA/PDPA) shown in Scheme 1. [c] Weight percent of pinanylsilyl group in polymer. [d] Determined by GPC (eluent = THF; polystyrene standard). [e] In chloroform (*c* 0.03−0.06 g/dL). [f] Permeation coefficient. [g] Enantiomeric excess of permeate was determined by HPLC with an optical resolution column (CROWNPAK CR; eluent, aq. HClO_4pH 1.0). [h] Polymerized at 80 °C for 3 h. [i] Permeation of racemic 2-BuOH. Enantiomeric excess of permeate was determined by HPLC with an optical resolution column (CHIRALCEL OD-H; eluent, *n*-hexane/2-PrOH = 9:1 (v/v)).

where.[12] The polymers were isolated by precipitation into a large amount of methanol and polymer yields were determined by gravimetry. The molecular weights of polymers were determined by gel permeation chromatography calibrated by standard polystyrene (eluent: THF). Free-standing membranes of the obtained polymers were fabricated by casting toluene solution of the polymers. "*Depinanylsilylation*" of the membranes was carried out by exposure of the membranes into a mixture of hexane/trifluoroacetic acid (volume ratio 1:1) at room temperature for 3 days following methods in the literature.[9,13] Enantioselective permeabilities were investigated by permeations of racemic tryptophan (0.5 wt % aqueous solution, concentration-driven permeation method), and 2-butanol (2-BuOH) (pervaporation method).[14]

Results and Discussion. In our previous study, PDPA, polymerized by TaCl_5−n-Bu_4Sn gave a high-molecular-weight polymer in high yields.[8] On the other hand, in a preliminary experiment, homopolymerization of PPDPA gave only a low molecular-weight polymer ($M_n = 2900$) in a low yield. This result is attributable to the steric hindrance from the two pinanylsilyl groups at the *meta* and *para* positions on each phenyl ring. To synthesize poly(diphenylacetylens) having a high content of pinanylsilyl group, copolymerization of PPDPA with PDPA was examined (Table 1). At 30 and 40 of PPDPA mol % in the feed, copolymerization proceeded smoothly to give copolymers having M_w of 4.2×10^5 (poly(**1**)) and 3.7×10^5 (poly(**2**)), respectively, in moderate yields (Table 1, runs 1, 2). Pinanylsilyl group content (Pi) of poly(**1**) and poly(**2**) increased to 57.7 and 59.9 wt %, respectively, compared with poly(**3**) [PDPA homopolymer] (Table 1, run 3). All polymers displayed very large optical rotations and intense large Cotton effects[7] in the CD spectra that is attributable to the backbone π−π^* transition. For example, poly(**1**) and poly(**2**) showed $[\alpha]_D$ of +428 and +876°, respectively. These results indicate that the main chains of the present polymers exist in a predominantly one screw sense. All polymers gave free-standing membranes by solution casting, and the "*depinanylsilylation*" was carried out in accordance with the literature method.[9,13] "*Depinanylsilylation*" proceeded quantitatively, and completion of the reactions was confirmed by IR spectra of the membranes before and after the reaction. Thus, the characteristic absorptions at 3060 ($\delta_{\text{s,aliphatic C−H}}$), 1250 ($\delta_{\text{s,SiC−H}}$), 1119 ($\nu_{\text{as,Si−CH}_3}$), 855 ($\nu_{\text{as,Si−CH}_3}$), and 812 ($\nu_{\text{s,Si−CH}_3}$) cm^{-1} completely disappeared in the IR spectrum of a polymer membrane, which agreed well with that of poly(diphenylacetylene) synthesized directly by polymerization.

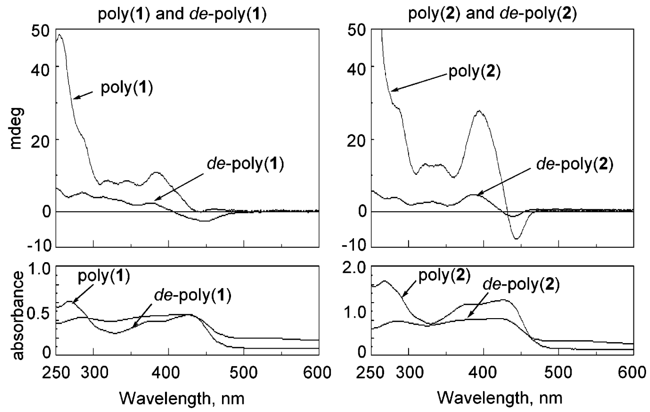

Figure 1. CD and UV−vis spectra of the polymers before and after depinanylsilylation in membrane: (left) poly(**1**) and *de*-poly(**1**); (right) poly(**2**) and *de*-poly(**2**).

Figure 1 illustrates CD and UV−vis spectra of polymer membranes before and after "*depinanylsilylation*". The depinanylsilylated poly(**1**) [*de*-poly(**1**)] and the depinanylsilylated poly(**2**) [*de*-poly(**2**)] showed CD signals similar to those of the original polymers (poly(**1**) and poly(**2**)) in the UV−vis region.[15] This fact indicates that the depinanylsilylated polymer retains the same one-handed helical conformation as in the original polymer.[16] As a result, polymer membranes containing only a one-handed helical conformation as the chiral source were obtained. It is very interesting to clarify the enantioselective ability of these membranes.

To elucidate the enantioselective ability of the depinanylsilylated membranes, enantioselective permeations of racemic tryptophan (0.5 wt % aqueous solution; concentration-driven permeation) were examined. The results of permeation through the depinanylsilylated membranes and the original membranes for comparison are summarized in Table 1. Interestingly, all the depinanylsilylated membranes could separate enantioselectively via permeation of an aqueous solution of racemic tryptophan to give an (*R*)-isomer enriched permeate (Table 1, runs 1−3). This finding is the first example of enantioselective permeation through a chiral polymer membrane having only a one-handed helical conformation as chiral source. The enantiomeric excesses (% ee) of permeate through *de*-poly(**1**), *de*-poly(**2**), and *de*-poly(**3**) were 10.1, 15.2, and 48.5, respectively. These values slightly decreased compared with that of the original polymers (poly(**1**), 16.4; poly(**2**), 23.1;

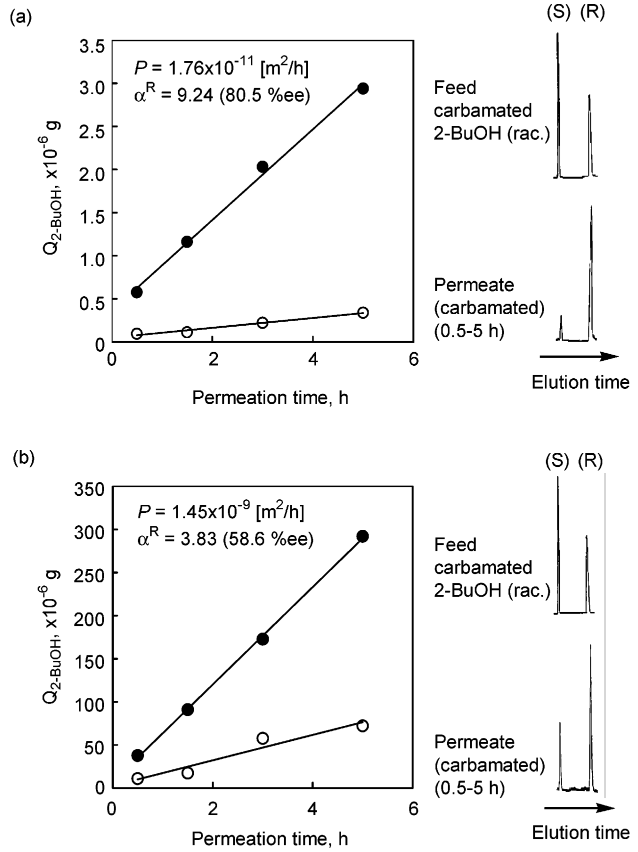

Figure 2. (Left) Plots of quantity ($Q_{2-\mathrm{BuOH}}$) of permeated (●)−(R)−(+)- and (○)−(S)−(−)-2-BuOH vs permeation time through (a) poly(**3**) membrane (top) and (b) *de*-poly(**3**) membrane (bottom), respectively. (Right) HPLC chromatogram of carbamated 2-BuOH. Conditions: column, CHIRALCEL OD-H; eluent, *n*-hexane/2-PrOH = 9:1 (v/v).

poly(**3**), 54.3). Permeation coefficients (*P*) of the depinanylsilylated membranes were about 4 times as large as those of the original polymers. The highest value of *P* was 22.5 × 10^{-12} m^2/h for *de*-poly(**1**) prepared from a membrane with the highest content of pinanylsilyl group, and the increasing order of *P* for the depinanylsilylated membranes is *de*-poly(**3**) < *de*-poly(**2**) < *de*-poly(**1**), which clearly corresponds with that of pinanylsilyl content (Pi). This fact indicated that the molecular-scale voids generated by "*depinanylsilylation*" are indeed reproducibly retained.

2-BuOH is a small and less polar molecule and the direct separation of the racemate by chiral HPLC is impossible at present. For this reason, it is very significant to examine enantioselective permeation of racemic 2-BuOH by using the new chiral membranes. Figure 2 shows the normalized quantity (*Q*) of permeated (*R*)- and (*S*)-2-BuOH vs permeation time through *de*-poly(**3**) and poly(**3**) in pervaporation[14,17] when racemic 2-BuOH was supplied. In both pervaporations, the (*R*)-isomer preferentially permeated, and the % ee values of permeate for *de*-poly(**3**) were 58.6 in good selectivity (poly(**3**): 80.5% ee) (Table 1, run 4). The effect of depinanylsilylation on *P* was very significant in pervaporation of 2-BuOH, *P* of *de*-poly(**3**) was increased about 2 orders of magnitude over *P* of poly(**3**). These results strongly indicate that molecular-scale voids generated by "*depinanylsilylation*" remain and a chiral helical structure in polymer membrane is effective for enantioselective permeation.

In summary, we prepared the polymer membranes having only one-handed helical conformation as chiral source by "*depinanylsilylation*" of poly(diphenylacetylenes) with high content of the pinanylsilyl group, which were synthesized by copolymerization of 1-phenyl-2-[4-(dimethyl(10-pinanyl)silyl)phenyl]acetylene (PDPA) with 1-[3-(dimethyl(10-pinanyl)silyl)phenyl]-2-[4-(dimethyl-(10-pinanyl)silyl)phenyl]acetylene (PPDPA). We found enantioselective permeabilities of the membranes having only main chain chirality for the first time. It was clarified that "*depinanylsilylation*" is effective for permeability enhancement because of the molecular-scale voids generated by "*depinanylsilylation*". Investigation of the mechanism for enantioselective permeation and imprint effect[18,19] is now in progress.

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(15) CD measurement: The membrane was prepared by casting a toluene solution of the polymer onto a quartz plate, and depinanylsilylation was carried out according to the literature method.[8,10] Then, the thin polymer membrane on quartz plate was used for CD measurement. The influence of birefringence is denied for the present solid state CD spectrum because it hardly changed with measuring conditions.

(16) It is assumed that the chiral memory in this paper is attributable to the low flexibility of the polymer chain. In general, the T_g values of poly(diphenylacetylenes) are fairly high, and no glass transition is observed below the onset temperature of thermal decomposition. Also, no polymers in this paper indicated the T_g below their decomposition temperature (ca. 270 °C).

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MA035493H