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Top-Down Preparation of Self-Supporting Supramolecular Polymeric Membranes Using Highly Selective Photocyclic Aromatization of Cis–Cisoid Helical Poly(phenylacetylene)s in the Membrane State

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Ⓢ *Supporting Information*

ABSTRACT: A novel, highly selective photocyclic aromatization (SCAT) of π-conjugated polymers from phenylacetylene having two hydroxyl groups to exclusively yield a 1,3,5-trisubstituted benzene derivative was developed, and its success was confirmed by ^{1}H NMR, GPC, and TOF-MS. The SCAT reaction has many unique characteristics. (1) It is a quantitative reaction: it gave only the corresponding cyclic trimer, i.e., a 1,3,5-trisubstituted benzene derivative, quantitatively (100%). No byproducts were produced under the best conditions. (2) It is an intramolecular reaction: it occurred between three adjacent monomer units in one macromolecule. (3) It is a stereospecific and topochemical or template reaction: the reactivity strongly depended on the configuration and conformation of the starting polymer substrates. (4) It is a photoreaction: high selectivity (100%) was observed only by the use of visible light irradiation, not by heating. (5) It is a solid-state reaction: high selectivity (100%) was observed only in the solid state, not in solution. *In addition,* (6) the resulting cyclic trimers could form a self-supporting membrane, despite their low molecular weights. This new approach resulted in a new class of supramolecular polymers consisting of a 1,3,5-trisubstituted benzene derivative, numbers of which were linearly linked by hydrogen bonds and stacked benzene derivatives. Since SCAT has such high selectivities and is useful for the preparation of a self-supporting supramolecular polymer membrane, many applications can be expected.

Although many supramolecular polymers have been reported,[1,2] only a few of them are strong enough to be used as structural materials. For example, one is three-dimensionally connected by multiple hydrogen bonds and not linear but a network polymer;[3,4] another contains covalent polymer parts and is not prepared from a low-molecular-weight compound.[5] Since generally supramolecular polymers are prepared from solution,[1−6] monomers and their supramolecular polymers are limited in variety because the monomer structures must promote the production of the supramolecular structure. The solution method is a bottom-up approach, where the supramolecular structures are governed by the molecular structure of the monomers. To overcome this limitation, another approach is needed, such as a template method in the solid state.

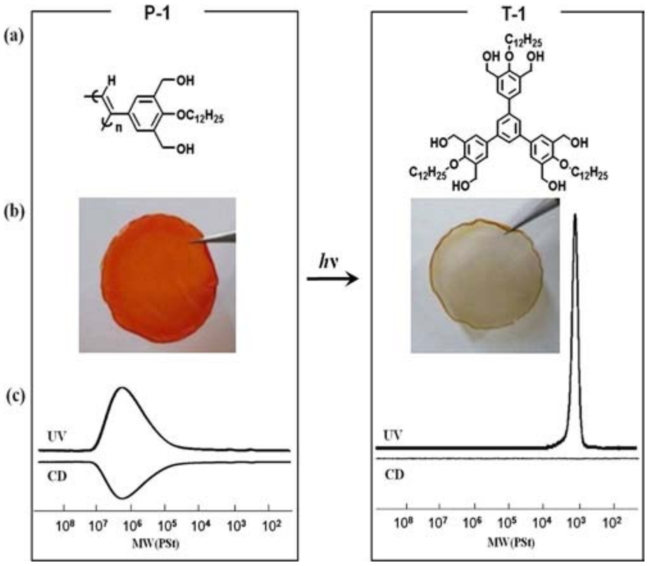

Figure 1. SCAT of **P-1** to **T-1** (Table 1, no.1): (a) chemical structures of starting polymer **P-1** and SCAT product **T-1**; (b) photographs of **P-1** (a polymer membrane) and **T-1** (a supramolecular polymer membrane); (c) GPC curves detected by UV and CD of **P-1**[21] and **T-1**.

In general, poly(substituted acetylene)s[7−10] are degraded by heating in nonselective reactions, giving many decomposition compounds having complex structures.[11−14] During our experiments on permeation through membranes composed of poly(substituted acetylene)s,[15−20] we discovered highly selective decomposition reactions that yield low-molecular-weight com-

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Scheme 1. Mechanism of SCAT Reaction: (a) 6π Electrocyclization (First Step) and (b) Aromatization with Degradation (Second Step)

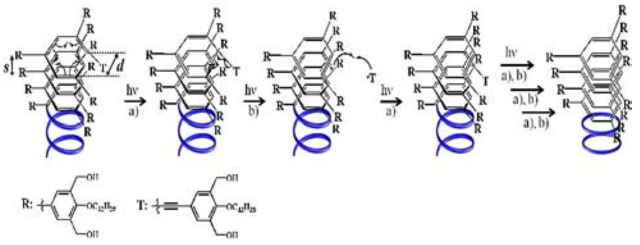
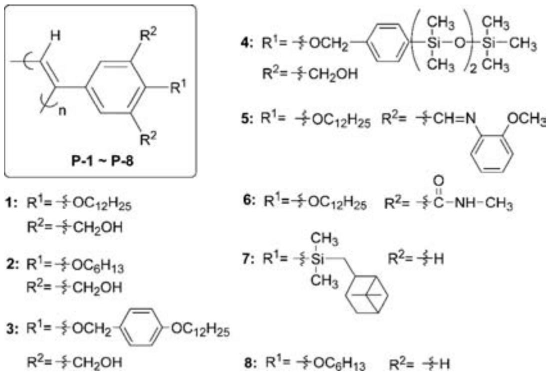


Chart 1. Starting Poly(phenylacetylene)s (P-1~P-8) for SCAT



pounds (see Figures 1 and SA-1,2).[21] Surprisingly, the resulting compound still had the ability to form a self-supporting membrane (Figures 1 and 2). This is a new approach for preparation of supramolecular linear polymers, i.e., a top-down preparation method different from the conventional solution method. Here we report the discovery of a novel polymer reaction that offers high selectivity and self-membrane-forming ability of the resulting supramolecular polymer.

A novel, highly selective photocyclic aromatization reaction (SCAT, Scheme 1) of a red π-conjugated polymer (**P-1** in Chart 1 and Figure 1)[11,12,20] from a phenylacetylene having two hydroxyl groups and a dodecyloxy group to exclusively yield a noncolored 1,3,5-trisubstituted benzene derivative (**T-1** in Figure 1) was confirmed by GPC (Figures 1 and SB), ^{1}H NMR (Figures SC and S1-1-10), and TOF-MS (Figure S1-1-11). The reaction was almost quantitative because it gave only the corresponding cyclic trimer, a 1,3,5-trisubstituted benzene derivative, with no byproducts under the best conditions, i.e., visible light irradiation in the membrane state (see SI[2]-2.1 for details of the SCAT procedure), as shown in Table 1, no. 1.

The SCAT reaction is strongly dependent on the chemical structure of the starting monomers, which determines the configuration and conformation of the resulting polymers (for polymerization of **1**–**8**, see SI[2]-1.2). For example, **P-2**, **P-3**, and **P-4**, prepared from the corresponding monomers having two hydroxyl groups, produced **T-2**, **T-3**, and **T-4**, respectively, in high selectivities (95–100%). In other words, the SCAT reaction proceeded (Figures 2 and SA-1,2 and Table 1, nos. 9–11) the same as for **P-1**. On the other hand, no SCAT reaction proceeded from the monomers having no hydroxyl groups, i.e., **P-5**, **P-6**, **P-7**, and **P-8** (Table 1, nos. 12–15). In other words, the polymers from monomers having two hydroxyl groups were SCAT-active, and the others were inactive. This may be because the polymers from the corresponding monomers having two hydroxyl groups adopted tighter helical structures based on the cis–cisoidal(c-c) conformation (details below). Therefore, the SCAT reaction can be categorized as a topochemical or template reaction.

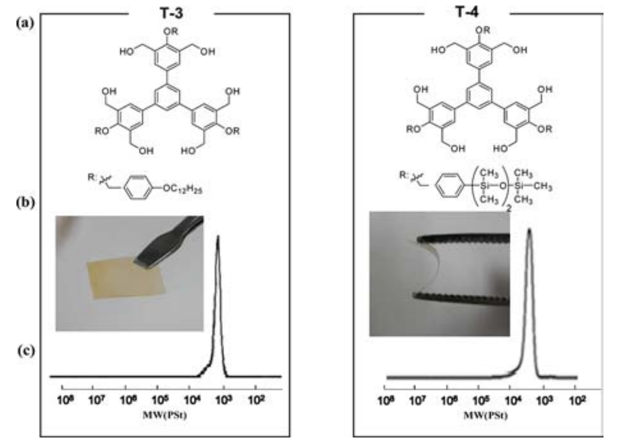


Figure 2. (a) Structures of **T-3** (Table 1, no. 10) and **T-4** (Table 1, no. 11). (b) Photographs of the supramolecular polymer membranes of **T-3** and **T-4**. (c) GPC curves of **T-3** and **T-4** (see Figure SA-1,2).

We assumed the key to a structure's suitability for SCAT was not the chemical structure of the monomers (polymers) but the conformation and configuration of the main chain of the starting polymers. To check this, we examined the SCAT activities and selectivities of polymers having different conformations and configurations (Table 1, nos. 2–4) formed from the same monomer, **1**. (For preparation of c-t and t-c **P-1**, see SI[2]-1.3 and Figure SD.) As expected, only **P-1**, with a cis–cisoidal (c-c) helical structure, was SCAT-active; the others, with cis–transoidal (c-t) or trans–cisoidal (t-c) helical structure, were SCAT-inactive. Therefore, the SCAT activity was determined by the conformation and configuration of the starting polymers; i.e., c-c polymers are suitable as substrates for SCAT.

High selectivity (100%) was observed only by visible light irradiation, but not by heating (Table 1, no. 5), and only in the solid state, not in solution (Table 1, no. 6) (the reason is discussed below). Since the SCAT reaction occurs by light irradiation in the membrane state, it should offer a promising approach to precisely controlled membrane structures, such as asymmetric membranes and channel-containing membranes.

In addition to the high selectivities observed, the resulting cyclic trimers were able to form self-supporting membranes, despite their low molecular weights. The products are a new class of supramolecular polymers consisting of the 1,3,5-trisubstituted benzene derivatives linked *linearly* by hydrogen bonds and benzene stacking. Since the supramolecular polymer **T-1** with self-supporting membrane-forming ability could not be prepared from a solution of **T-1** (Figure 3, **T′-1**), it was apparent that the supramolecular polymers can be prepared only by an *in situ* SCAT method. This is a new approach for preparation of a new class of linear supramolecular polymers, i.e., a top-down preparation method different from the conventional solution method, the so-called the bottom-up method.[1−6]

As mentioned above, the SCAT reaction and its products have very interesting and important features. To understand why such phenomena occurred and to apply the SCAT reaction and its products more effectively, we need to understand the reaction mechanism and the relationship between the structures of the starting covalent polymer (**P-1**)[15,16] and the SCAT product, a

Table 1. Characterization of Starting Polyphenylacetylenes (P-1~P-8) and Results of SCAT Reaction[a]

	starting polymer (**P-1**–**P-8**) for the SCAT reaction								results of SCAT reaction[a]			
				λ_{max} (nm)								
no.	polymer[b]	M_w[c] ($\times10^{-5}$)	cis (%)[d]	UV[e]	DR-UV[f]	DSC[g] (°C)	main chain[h]	state	conversion[c] (%)	selectivity[c] (%)	product[b,i]	SI[1]-
1	**P-1**	25	97	298	510	–, 235	c-c	membrane	100	100	**T-1**	(2)
2	**P-1**	25	97	270, 450	448	120, 230	c-t[j]	membrane[j]	0	0	–	(3)
3	**P-1**	25	97	270, 448	–	–	c-t[k]	membrane[k]	0	0	–	(4)
4	**P-1**	25	97	–	602	no peaks	t-c (t-t)	membrane	0	0	–	(5)
5	**P-1**	25	97	298	510	–, 235	c-c	membrane[l]	100	50	**T-1**	(6)
6	**P-1**	25	97	298	510	–	c-c	solution[m]	100	19	**T-1**	(7)
7	**P-1**	22	97	298	512	–	c-c	bl. membr.[n]	100	100	**T-1**	–
8	**P-1**	0.072	100	298	500	–, 235	c-c	membrane	100	100	**T-1**	–
9	**P-2**	–[o]	–[o]	–[o]	510	–, 225	c-c	powder[o]	100	100	**T-2**	(8)
10	**P-3**	61	89	298	515	–, 205	c-c	membrane	100	95	**T-3**	(9)
11	**P-4**	400	89	298	–	–	c-c	membrane	100	95	**T-4**	(10)
12	**P-5**	35	–	250, 497	–	–	c-t	membrane	0	0	–	(11)
13	**P-6**	97	–	280, 530	–	–	c-t	membrane	0	0	–	(12)
14	**P-7**	1.1	96	–	460	110, 214	c-t	membrane	0	0	–	(13)
15	**P-8**	0.31	99	–	565	–, 168	c-c	powder	0	0	–	(14)

[a] By visible light irradiation under nitrogen at 25 °C; see SI[2]-2. [b] For the code, see Chart 1. [c] By GPC (polystyrene standard). [d] By ^{1}H NMR. [e] In solution. [f] Membranes; see Figure 3. [g] See SI[1], Figure SD. [h] c-c = cis–cisoid, c-t = cis–transoid, t-c = trans–cisoid, and t-t = trans–transoid; for the determination, see SI. [i] See Figures 1 and 2. [j] For the preparation of c-t **P-1**, see SI. [k] Prepared from pyridine solution. [l] By heating instead of visible light irradiation. [m] In chloroform. [n] Polystyrene-based blend membrane. [o] Insoluble polymer.

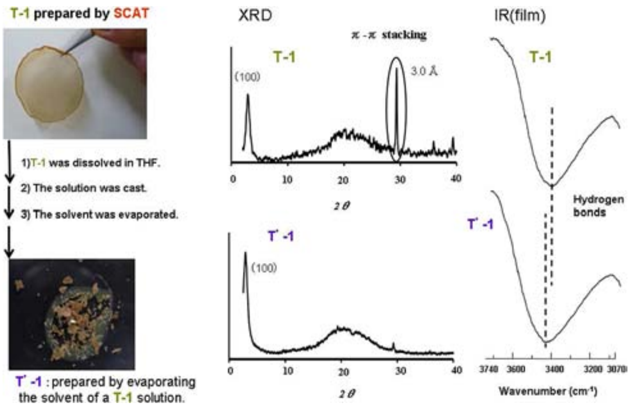


Figure 3. Photos, XRD, and IR of **T-1** membrane and **T′-1**.[22]

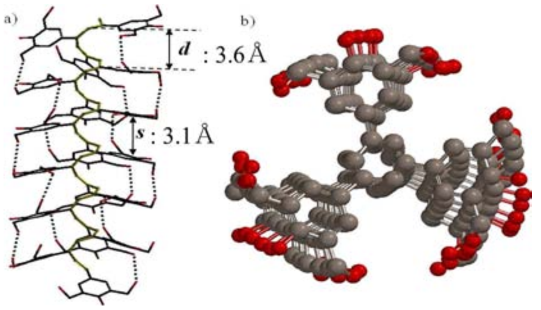


Figure 4. 3D chemical structure of **P-1** with intramolecular hydrogen bonds between the *m* and *m*+3 monomer units: (a) side view and (b) top view (dodecyl groups are omitted for clarity). *d*, distance between the carbons that can bond in the SCAT reaction; *s*, stacking distance.

supramolecular polymer (**T-1**). As we discussed above, SCAT is a topochemical or template reaction. In other words, the c-t poly(phenylacetylene)s such as **P-5**, **P-6**, and **P-7** are not suitable for SCAT, while c-c structures of poly(phenylacetylene)s[21] such as **P-1**, **P-2**, **P-3**, and **P-4** are suitable for SCAT. (The 3D molecular structure of c-c **P-1** is shown in Figure 4, determined by a molecular calculation.) However, even a poly(phenylacetylene) having a c-c structure was not suitable for SCAT (**P-8**, Table 1, no. 15). To understand the strong and critical dependence of the configuration and conformation of the helical main chain of the starting polymers on the SCAT reaction, the distances (*d*/Å in Figure 4) between the carbons that can make covalent bonds in the SCAT reaction were estimated by a molecular calculation (Table S1 and SI[2]-3).[22] The results indicate that the *d* of **P-1** (3.85 Å) is within 4.0 Å and shorter than that of **P-8** (4.08 Å), due to differences in the helical pitch and the dihedral angles. A similar dependency was reported in a different 6*π* electrocyclic ring-closing photoreaction by Irie et al.,[23] confirming the critical need for a tighter helical structure for a SCAT reaction to be successful.

Judging from the changes in the GPC traces during the SCAT reaction (Figure SB), the reaction started at the ends of the macromolecules. To pursue this hypothesis, the *d* values at the internal and terminal positions of the macromolecules of **P-1** were estimated by a molecular calculation (SI[2]-3), which showed that the *d* values at the terminal positions were shorter than those at the internal positions (Table S1). Therefore, the reactivity at the end positions was found to be higher. This result supports the end-initiating mechanism proposed in Scheme 1.[24] In summary, the most important factor contributing to a high reactivity for the SCAT reaction is a small separation between the two carbons that will form a bond by the SCAT mechanism at the end position. However, generally the conformations of the end groups are not rigid but flexible. In the solid state, the motion was suppressed; therefore, the suppressed motion made the SCAT reaction possible only in the solid state, but not in solution.

The SCAT reaction does not occur on heating but only on photoirradiation. Because the first step of SCAT is a 6*π* electrocyclic ring-closing reaction, the Woodward–Hoffmann rule can be applied. By photoirradiation of **P-1**, ring-closing can occur via a conrotatory process, while by heating **P-1**, ring-closing can occur via a disrotatory process. In the SCAT reaction, one of the two substituents on the two carbons that are joined in the electrocyclic reaction is a polymer chain; i.e., it is very bulky. Therefore, the possibility of the SCAT reaction occurring by heating is low; in general, high steric repulsion occurs in disrotatory processes. In addition, the results of calculations indicated that the cyclic compounds prepared by heating had a larger strain than those made by photoirradiation and the planarity of the cyclohexadiene intermediate formed by photoirradiation was higher. Thus, the aromatization step, i.e., the second step in the SCAT reaction after photocyclization, is much easier than that by heating.[24,25] Scheme 1 summarizes the mechanism.

The self-supporting membrane properties of the supramolecular polymers prepared by SCAT reaction of **P-1** are thought to be due to hydrogen bonds within the column and stacking of the benzene derivatives in the direction of the column.[26] This arises because the original polymer **P-1**, which had hydrogen bonds (m and m+3) within the macromolecules and stacking of the phenyl pendant groups in the direction of the macromolecules, acted as a template. In fact, when the solvent was evaporated from a solution of **T-1** which had been isolated once, only a powdery solid was obtained (Figure 3, **T′-1**). This was supported by XRD and IR of **T-1** and **T′-1** (Figure 3). In addition, supramolecular polymer membranes formed from starting polymers having higher molecular weights had higher mechanical strengths (Table S2). This is because supramolecular polymers from starting covalent polymers having a higher molecular weight contain higher degrees of hydrogen bonding and stacking.

In conclusion, a novel, highly selective method for the photocyclic aromatization (SCAT) of π-conjugated polymers from phenylacetylene having two hydroxyl groups was found to yield exclusively a 1,3,5-trisubstituted benzene derivative. The SCAT reaction was highly selective and specific, and the resulting cyclic trimers formed self-supporting membranes, despite their low molecular weights. The products are members of a new class of supramolecular linear polymers consisting of the 1,3,5-trisubstituted benzene derivative linearly linked by hydrogen bonds and benzene stacking. Since this SCAT reaction has several high selectivities and is photoreaction in the membrane state, many kinds of applications are expected. For example, the microstructures of starting polymers that are difficult to be determined by NMR can be clearly determined by investigating the structures of the corresponding SCAT products. Precise selective modification of membranes of the starting polymers can be performed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

GPC, NMR, DR-UV, and XRD characterization data, and experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) de Greef, T. F. A.; Smulders, M. M. J.; Wolffs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687.

(2) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.

(3) de Greef, T. F. A.; Meijer, E. W. *Nature* **2008**, *453*, 171.

(4) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.

(5) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874.

(6) Yoshikawa, I.; Sawayama, J.; Araki, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1038.

(7) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102.

(8) Percec, V.; Aqad, E.; Peterca, M.; Rudick, J. G.; Lemon, L.; Ronda, J. C.; De, B. B.; Heiney, P. A.; Meijer, E. W. *J. Am. Chem. Soc.* **2006**, *128*, 16365.

(9) Lai, L.; Lam, J. W. Y.; Cheuk, H. K. K. L.; Sung, H. H. Y.; Williams, I. D.; Tang, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3701.

(10) Shirakawa, Y.; Suzuki, Y.; Terada, K.; Shiotsuki, M.; Masuda, T.; Sanda, F. *Macromolecules* **2010**, *43*, 5575.

(11) Percec, V.; Rudick, J. G. *Macromolecules* **2005**, *38*, 7241.

(12) Percec, V.; Rudick, J. G.; Nombel, P.; Buchowicz, W. *J. Polym. Sci., Part A: Polym. Chem* **2002**, *40*, 3212.

(13) Matsunami, S.; Watanabe, T.; Kamimura, H.; Kakuchi, T.; Ishii, F.; Tsuda, K. *Polymer* **1996**, *37*, 4853.

(14) Deng, J.; Tabei, J.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Polymer* **2004**, *45*, 7395.

(15) Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6346.

(16) Liu, L.; Zang, Y.; Hadano, S.; Aoki, T.; Teraguchi, M.; Kaneko, T.; Namikoshi, T. *Macromolecules* **2010**, *43*, 9268.

(17) Aoki, T.; Kokai, M.; Shinohara, K.; Oikawa, E. *Chem. Lett.* **1993**, 2009.

(18) Aoki, T.; Kaneko, T. *Polym. J.* **2005**, *37*, 717.

(19) Aoki, T.; Kaneko, T.; Teraguchi, M. *Polymer* **2006**, *47*, 4867.

(20) Zang, Y.; Aoki, T.; Liu, L.; Abe, Y.; Kakihana, Y.; Teraguchi, M.; Kaneko, T. *Chem. Commun.* **2012**, *48*, 4761.

(21) Polymers **P-1**−**P-5** were prepared by helix-sense-selective polymerization and therefore have chiral structures, i.e., one-handed helical main chains.

(22) The unusual small distance s of the stacking was thought to cause this unexpected reaction, SCAT of **P-1**, and the unusual higher strength of **T-1**. Actually, **P-8**, whose stacking distance is 3.4 Å, has no SCAT reactivity (see Table S1).

(23) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, *73*, 2804.

(24) We could not detect the intermediate 1,3-cyclohexadiene residues in **P-1** by NMR. This may be because the aromatization step (the second step) was very rapid and the first step (6π-electrocyclization) was the rate-determining step. Since cyclization is the rate-determining step in this depolymerization reaction, it was thought that the terminal positions, where the cyclization occurs more easily, have higher SCAT reactivities than the internal positions.

(25) Srinivasan, R. *J. Am. Chem. Soc.* **1960**, *82*, 5063.

(26) Since **T-1**−**T-4**, showing self-standing membrane-forming ability, have no functional groups in the side chains (R^1 in Chart 1) that make strong interactions, such as hydrogen bonds, between them, the strength was thought to be due to the hydrogen bonds and stacking of the core parts, i.e., the benzene derivatives having six hydroxyl groups within columns.