Fluoro-functionalized Molecularly Imprinted Polymers Selective for Herbicides

Jun Matsui, Yoko Miyoshi, and Toshifumi Takeuchi*
Laboratory of Synthetic Biochemistry, Faculty of Information Sciences, Hiroshima City University, 151-5 Ozuka, Numata-cho, Asaminami-ku, Hiroshima 731-31

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Polymers molecularly imprinted against a herbicide prometryn were prepared using (2-trifluoromethyl)acrylic acid (TFMAA) as a new monomer to construct complementary binding sites within the polymers. In chromatographic studies, the polymers with TFMAA exhibited higher affinity and selectivity for the template prometryn than those prepared with a conventional monomer methacrylic acid (MAA).

Molecular imprinting is a technique for preparing synthetic polymers possessing recognition sites complementary to a template substance.[1-3] Over the past decade, molecularly imprinted polymers have been shown to be useful as tailor-made affinity elements for chromatographic stationary phases,[4-7] metal ion-selective matrices,[8,9] antibody mimics[10,11] and enzyme mimics.[12-14] In the molecular imprinting procedures, functional monomers, possessing both functionalities for interacting with a template molecule and polymerizable vinyl groups, result in functional residues as center of binding sites in the resulting polymer. Therefore, the selection of functional monomers which interact strongly with a template is crucial to generate high affinity binding sites. To date, several functional monomers have been reported for use in molecular imprinting, being classified into two groups. One is a monomer with a functional group forming a reversible covalent binding to the template, such as ester and ketal bonds.[3,15,16] The other general type uses non-covalent binding to the template, such as hydrogen bonding and ionic interactions. The non-covalent approach currently seems to be the more versatile, because it has a wider range of applications. Methacrylic acid (MAA), in particular, has been extensively utilized as a functional monomer in non-covalent molecular imprinting protocols.[1]

In this study we examined (2-trifluoromethyl)acrylic acid (TFMAA) as a new functional monomer for molecular imprinting. As the acidity of TFMAA is higher than that of MAA due to the strong electron withdrawing effect of the trifluoromethyl group, it possibly exhibits stronger interactions with a basic template. TFMAA is therefore expected to be a suitable functional monomer for imprinting basic substances. Prometryn, one of the s-triazine-type herbicides,[11] was tested as a model template in the imprinting system using TFMAA.

For the preparation of the prometryn-imprinted polymer with both TFMAA and MAA, **P(FM)**, 400 mg (1.67 mmol) of prometryn as a template was dissolved in 25 ml of chloroform. Into the solution, were added 935 mg (6.67 mmol, 4 eq.) of TFMAA and 288 mg (3.33 mmol, 2 eq.) of MAA as functional monomers, 9.35 g of ethyleneglycol dimethacrylate as a crosslinking agent and 120 mg of 2,2'-azobisisobutyronitrile as an initiator. The monomer mixture was placed under UV light (260 nm) at 3 °C for 12 h. The bulk rigid polymer obtained was ground (< 45 μm) and packed in a stainless steel column tube (150 mm x 4.6 mm i.d.). The column was washed exhaustively with methanol/acetic acid (4:1, v/v). A blank polymer **B(FM)** was prepared using the same recipe though without addition of the template. As references, two sets of polymers were also prepared in the same manner with the sole use of either TFMAA or MAA; prometryn-imprinted polymers, **P(F)** and **P(M)**, were prepared using TFMAA (1.403 g, 10.0 mmol, 6 eq.) and MAA (863 mg, 10.0 mmol, 6 eq.) as a functional monomer, respectively. The corresponding blank polymers, **B(F)** and **B(M)**, were prepared with the same amount of TFMAA and MAA.

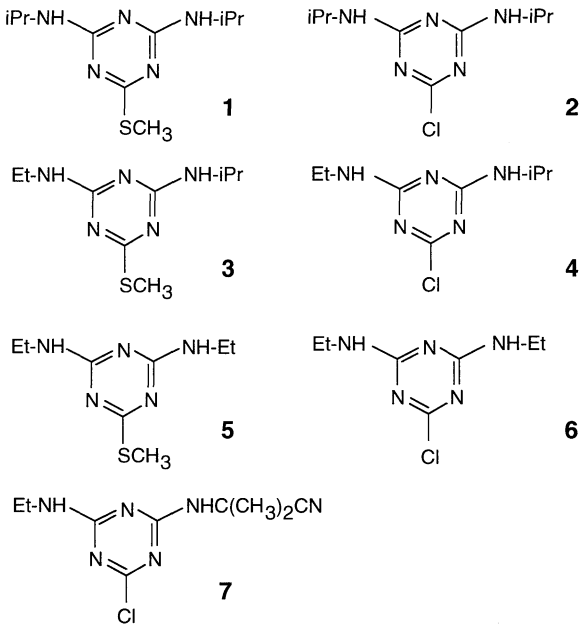

Figure 1. Structures of s-triazine-type herbicides tested: **1**, prometryn; **2**, propazine; **3**, ametryn; **4**, atrazine; **5**, simetryn; and **6**, simazine; **7**, cyanazine. Prometryn **1** was used as a template for the polymer preparation.

Chromatographic tests were performed using acetonitrile as an eluent at flow rate of 1.0 ml/min. Detection was carried out at 260 nm. Prometryn and other herbicides were used as samples (Figure 1). Capacity factors[6] were used for the evaluation of binding characteristics of the polymers.

The molecularly imprinted polymer **P(FM)** exhibited the selective binding to **1**, **3** and **5**. The retentions observed for those samples were much higher than those in **B(FM)**. Furthermore the longest retention was observed for the template **1** among them. These results demonstrate that the prometryn-imprinting successfully induced the enhanced binding ability for the template **1** into the EGDMA-TFMAA-MAA-copolymer. Because the structural differences among **1**, **3** and **5** are small, it can be concluded that considerably detailed size and shape informations had been imprinted in **P(FM)**. **P(FM)**, however, did not exhibit high selectivity to propazine **2** that bears the exactly same two isopropylamino groups as **1**. Since **2** bears a

Table 1. Capacity factors[a] for prometryn and other s-triazine-type herbicides

Sample	P(FM)	B(FM)	P(F)	B(F)	P(M)	B(M)
Prometryn **1**	26	(3.8)	9.7	(6.8)	2.3	(1.1)
Propazine **2**	1.2	(0.6)	0.6	(0.7)	1.2	(0.6)
Ametryn **3**	14	(3.7)	8.5	(6.6)	2.1	(1.1)
Atrazine **4**	1.0	(0.6)	0.5	(0.7)	0.9	(0.5)
Simetryn **5**	13	(3.4)	6.2	(5.6)	1.7	(1.0)
Simazine **6**	0.9	(0.5)	0.4	(0.6)	0.7	(0.5)
Cyanazine **7**	0.4	(0.3)	0.2	(0.3)	0.4	(0.3)

[a] Average data of the duplicated measurments are listed.

chloro group instead of a methylthio group, it is less basic than **1**. This suggests that high basicity of the amino groups is an essential factor for the recognition. Also in the blank polymer **B(FM)**, **1**, **3** and **5**, bearing the methylthio group, were retained longer than the other four s-triazine derivatives. The results that the polymer retained the highly basic samples again imply that the retention mechanism is based on acid-base interactions.

Other herbicides and pesticides were also tested as LC samples to evaluate the selectivity of **P(FM)** (Table 2). For those species without an s-triazine structure, **P(FM)** showed no significant retentions, demonstrating the excellent selectivity of **P(FM)**.

Polymers prepared with TFMAA or MAA alone, **P(F)**, **B(F)**, **P(M)** and **B(M)** were also examined (Table 1). Among the three blank polymers, **B(F)** exhibited the strongest retention to s-triazine derivatives. The enhancement of the retention by the imprint effects, however, was much smaller than those observed in the **P(FM)** system. Although such imprint effects were also observed in **P(M)**, differences in the obtained capacity factors were insignificant. Consequently, **P(FM)** showed the highest affinity for the template **1** and the other s-triazine-type herbicides. Furthermore, **P(FM)** showed the best selectivity for **1** among the s-triazine-type herbicides, compared with the other two imprinted polymers. These results imply that different mechanisms (template-functional monomer interactions) are involved in MAA- and TFMAA-imprinting, and that those mechanism worked cooperatively to yield the high performance imprinted polymer **P(FM)**. It has been also reported[17] that atrazine (Figure 1) forms a complex with acetic acid through hydrogen bonding. For the complex formation, the ring nitrogen para to the chloro substituent and the side-chain amino group are involved in cooperative hydrogen bonding, whereby acetic acid acts as both a hydrogen bond donor and acceptor. Since MAA is expected to exhibit the hydrogen bonding as acetic acid does, MAA would interact with those functional groups of prometryn. However, it is still unsure how TFMAA interacts with prometryn, although TFMAA was shown to be suitable for developing the polymer that exhibit strong binding to the template. Detailed mechanism study and the optimization of the polymerization conditions using TFMAA are currently underway.

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Table 2. Relative Capacity Factors [a] in **P(FM)** for Prometryn and Reference Samples

Sample	Relative k'
Prometryn **1**	100
Alachlor	< 1
Anilazine	2
Asulam	< 1
Bentazon	1
Chlorpyrifos	< 1
Diazinon	< 1
Diuron	3
Flutranil	< 1
Isofenphos	< 1
MBPMC	< 1
MCP ethyl	< 1
Metribuzin	7
Pendimethalin	< 1
TPN	2

[a] The relative capacity factors were calculated by the equation, (k'_s / k'_p) x 100, where k'_s is the capacity factor for the sample and k'_p is for prometryn.

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