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H–D exchange reaction on benzene ring of polystyrene in hydrothermal deuterium oxide with platinum(IV) oxide catalyst

Mitsuru Yamamoto, Yutaka Yokota, Koichiro Oshima and Seijiro Matsubara*
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoutodaigaku-katsura, Nishikyo-ku, Kyoto 615-8510, Japan.
E-mail: matsubar@orgrxn.mbox.media.kyoto-u.ac.jp; Fax: +81-(0)75-383-2438; Tel: +81-(0)75-383-2441

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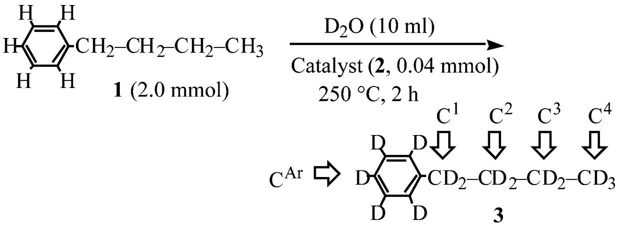
Benzene rings of polystyrene samples are labelled with deuterium oxide and catalytic amount of platinum(IV) oxide under hydrothermal conditions.

Deuterium labelled compounds have been important for both chemical and biological research and are mainly prepared by isotope exchange. A number of works concerning H–D exchange method have been reported. These works have been performed by acid catalysed reaction in D_2O,[1] base catalyzed reaction in D_2O,[2] and metal catalysed reaction under D_2 atmosphere.[3] It should also be noted that partial H–D exchange reactions were also performed under microwave irradiation[4] and under the effect of a transition metal catalyst in D_2O.[5] Recently, deuterated compounds have aroused interest not only for laboratory use but also for practical application. Deuterium labelled polymers are considered to be feasible materials for wave guides in optical communication, because of their transparency in the red beam infrared area of 500–800 nm.[6] In this case, a greater distribution of deuterium atoms in the polymer is preferable. The preparation of deuterium labelled polymers has been performed by polymerisation of labelled monomers. Direct H–D exchange has also been attempted in some cases. For example, active protons in a polymer such as N–H in polyamides were exchangeable with deuterium oxide.[7] The C–H bonds in a hydrocarbon skeleton were also attempted to be exchanged with D_2 gas in the presence of transition metal catalyst,[8] but the exchange ratio was quite low. Recently, we developed a new method of H–D exchange reaction of hydrocarbons with palladium catalyst under hydrothermal conditions with deuterium oxide.[9] In this method, hydrocarbons were heated with deuterium oxide and a palladium catalyst in a Teflon® lined stainless autoclave at 250 °C for several hours. Our developed method is easily applicable to various types of compounds. This hydrothermal method was applied to the deuterium labelling of polystyrene.

The efficiency of a catalyst for H–D exchange reaction of the aromatic ring was examined for the reaction of butylbenzene (**1**) as shown in Scheme 1. A mixture of butylbenzene (**1**, 2.0 mmol), 10 mol% catalyst, and deuterium oxide (20 g) in a 30 ml Teflon® vessel was placed in a stainless autoclave.[9–11] The whole was sealed and heated at 250 °C. The internal pressure reached to *ca.* 4 ~ 5 MPa. This hydrothermal condition was maintained for 2 h. The obtained mixture was extracted with hexane after cooling to room temperature. The extracts were concentrated and purified using short silica-gel column chromatography. The product was analyzed by GC , ^1H nmr, ^2H nmr, and mass spectra.

The use of Pd/C as a catalyst showed the best efficiency of H–D exchange on sp^3 carbons among the examined catalysts in Table 1.[9] As far as the exchange efficiency on the benzene ring of **1**, platinum(IV) oxide (PtO_2) gave the best result. In the deuteration of polystyrene, the efficiency on the benzene ring may have priority. As shown in Table 2, the conversion corresponding to the reaction time was examined. The H–D exchange on benzene ring was nearly completed after 14 h.



Scheme 1 H–D exchange reaction of butylbenzene (**1**).

As shown in Table 3, polystyrene samples were treated with hydrothermal deuterium oxide in the presence of catalytic amount of PtO_2. The samples were commercially available from Aldrich© as Mw standards of 800, 13000, 44000, and 280000. Polystyrene (2.0 g), PtO_2 (1.0 mmol), and deuterium oxide (2.0 g) were pulverized and mixed completely by a ball mill machine (planetary ball mill, P-5, Fritsch©, using a 80 ml stainless steel vessel and five

Table 1 Metal salt catalyzed deuteration of butylbenzene (**1**) under hydrothermal conditions[a],[b]

Run	Catalyst **2**	C^{Ar} (%)	C^1 (%)	C^2 (%)	C^3 (%)	C^4 (%)
1	Pd/C	20	67	42	49	43
2	PdO	2	61	38	50	42
3	PtO_2	28	42	26	32	30
4	Pd black	< 5	32	14	24	16
5	Raney Ni	3	28	10	13	5

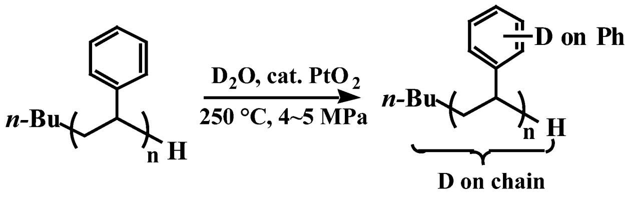
[a] Substrate (2.0 mmol), catalyst (2 mol% metal), and D_2O (20.0 g). [b] The ratios were determined by ^1H nmr, ^2H nmr, and mass spectra.

Table 2 PtO_2 catalyzed deuteration of butylbenzene **1** under hydrothermal conditions[a],[b]

Time (h)	C^{Ar} (%)	C^1 (%)	C^2 (%)	C^3 (%)	C^4 (%)
2	28	42	26	32	30
4	65	58	49	48	40
6	81	75	59	65	56
14	96	95	94	95	83

[a] Substrate (2.0 mmol), PtO_2 (2 mol%), and D_2O (20.0 g). [b] The ratios were determined by ^1H nmr, ^2H nmr, and mass spectra.

Table 3 Deuteration of polystyrene with D_2O-PtO_2.



Aldrich© Standard PS Mw	Reaction time (h)	D% on Ph	D% on Chain	Yield (%)
800	14	61	43	> 99
	100	71	52	> 99
13000	14	28	2	> 99
	100	42	7	> 99
44000	13	20	1	> 99
	100	44	3	> 99
280000	13	22	< 1	> 99
	100	38	2	> 99

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stainless steel balls (ϕ 20 mm)). The obtained mixture and deuterium oxide (15 g) in a 30 ml Teflon vessel was placed in a stainless steel autoclave. The autoclave was heated at 250 °C for the period indicated in Table 3. The internal pressure reached to *ca.* 4 ~ 5 MPa. The obtained mixture was extracted with chloroform after cooling to room temperature. The extracts were concentrated and purified by GPC (toluene on JAIGEL). The deuteration ratio was determined by ^{1}H nmr and ^{2}H nmr using bromoform and 1,1,2,2-tetrachloroetane-d_2 as internal standards. In the case of the reaction using molecular weight 800, the H–D exchange occurred on each carbon of the molecule. In the rather higher molecular weight samples in Table 3, the exchange efficiency decreased drastically on the carbon chain, but gently on the benzene rings. A tendency for the selective exchange on benzene rings was observed in this PtO_2 catalysed reaction.

The mass spectra of the deuterated polystyrene, obtained from the polystyrene Mw 800, PtO_2 catalyst, and D_2O was measured by MALDI-TOF (Voyager© Elite, dithranol/CF_3CO_2Ag). In Fig. 1, the spectra of the starting material (a) and of the deuterated material (b) are shown. While the peaks in Fig. 1 (a) were recorded every 104 *m*/*z* units, those in (b) were observed every 107 ~ 109 *m*/*z* units. This means that 3 ~ 5 D-atoms are substituted with H-atoms in the polystyrene, and is consonant with the result in Table 3. The spectrum in Fig 1 (b) did not show the existence of non-deuterated molecules. At least in this sample, the exchange occurred equally, but we cannot conclude homogeneity in the higher molecular weight samples at this moment.

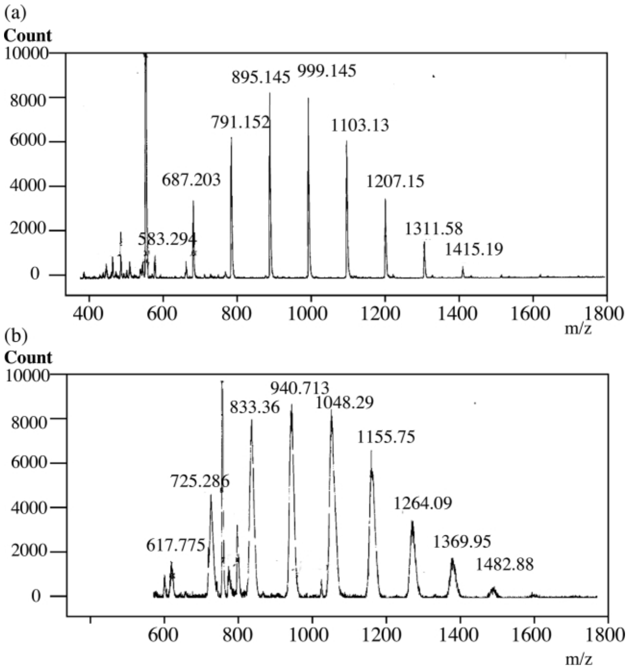

Fig. 1 MALDI-TOF mass spectra of polystyrene (Mw 800)/dithranol/ CF3CO_2Ag. (a) Before deuteration. (b) After deuteration.

Our developed hydrothermal deuteration with the assistance of a transition metal catalyst is easily applied to any substrate, as far as it is tolerant in 250 °C water. Although we have not examined mechanistic studies, we assume that the reaction proceeds *via* a platinum deuteride intermediate. The further application to various polymer deuteration is now underway.

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Notes and references

1 N. H. Werstiuk and T. Kadai, *Can. J. Chem.*, 1985, **63**, 530; N. H. Werstiuk and T. Kadai, *Can. J. Chem.*, 1974, **52**, 2169.

2 J. Yao and R. F. Evilia, *J. Am. Chem. Soc.*, 1994, **116**, 11229; T. Junk and W. J. Catallo, *Tetrahedron Lett.*, 1996, **37**, 3445.

3 J. G. Atkinson, M. O. Luke and R. S. Stuart, *Can. J. Chem.*, 1967, **45**, 1511.

4 J. R. Jones, W. J. S. Lockley, S.-Y. Lu and S. P. Thompson, *Tetrahedron Lett.*, 2001, **42**, 331; K. Fodor-Csorba, G. Galli, S. Holly and E. Gács-Baitz, *Tetrahedron Lett.*, 2002, **43**, 3789; J. M. Barthez, A. V. Filikov, L. B. Frederiksen, M.-L. Huguet, J. R. Jones and S.-Y. Lu, *Can. J. Chem.*, 1998, **76**, 726.

5 F. A. L. Anet and M. St. Jacques, *J. Am. Chem. Soc.*, 1966, **88**, 2585; J. L. Ganett and R. J. Hodges, *J. Am. Chem. Soc.*, 1967, **89**, 4545; O. Desponds and M. Schlosser, *Tetrahedron Lett.*, 1966, **37**, 47.

6 T. Kurihara, N. Ooba, S. Toyoda and T. Maruno, *Oyobuturi*, 2002, **71**, 1508; T. Kaino, K. Jinguji and S. Nara, *Appl. Phys. Lett.*, 1983, **42**, 567.

7 A. Koshino and T. Tagawa, *J. Appl. Polym. Chem. Sc.*, 1965, **9**, 117; M. S. Miller and I. M. Klotz, *J. Am. Chem. Soc.*, 1973, **95**, 5694.

8 J. D. Tanzer and B. Crist, Jr., *Macromolecules*, 1985, **18**, 1291; L. C. Case and J. D. Atlas, *J. Polym. Sci.*, 1960, **45**, 435.

9 S. Matsubara, Y. Yokota and K. Oshima, *Chem. Lett.*, 2004, **33**, 294(web released May 15). S. Matsubara, Y. Yokota and K. Oshima, *Org. Lett.*, 2004, **6**, 2071.

10 D. Bröll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel and P. Zehner, *Angew. Chem. Int. Ed.*, 1999, **38**, 2998; N. Akiya and P. E. Savage, *Chem. Rev.*, 2002, **102**, 2725; P. E. Savage, *Chem. Rev.*, 1999, **99**, 603.

11 Y. Yamasaki, H. Enomoto, N. Yamasaki and M. Nakahara, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2687; B. K. Mehta, K. Yanagisawa, M. Shiro and H. Kotsuki, *Org. Lett.*, 2003, **5**, 1605.