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Novel solid-state polycondensation I. Oxidative-coupling polymerization of 2,6-dihydroxynaphthalene†

Masato Suzuki* and Yutaka Yatsugi

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, and International Research Center of Macromolecular Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan. E-mail: msuzuki@polymer.titech.ac.jp; Fax: 81 3 5734 2888; Tel: 81 3 5734 3552

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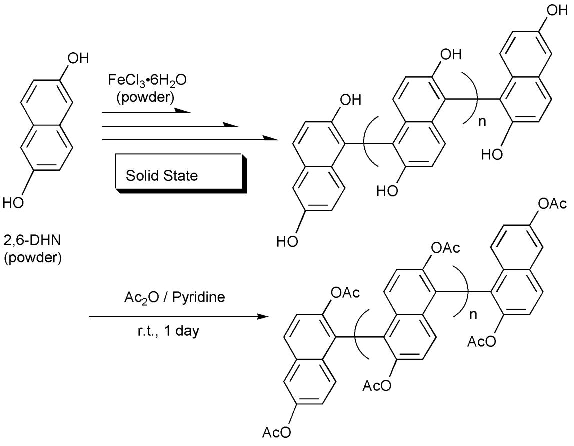
Grinding crystals of 2,6-dihydroxynaphthalene–benzylamine complex with $FeCl_3 \cdot 6H_2O$ powder in a mortar resulted in the 1,5-oxidative-coupling polymerization of 2,6-dihydroxynaphthalene at room temperature

Solid-state polymerization is not a widely used technique, but, unexpectedly, there are a number of polymerisations that take place in the solid state: for instance, addition polymerization of unsaturated monomers, ring-opening polymerization, polycondensation, and [2 + 2] polyaddition.[1,2] In some cases, solid-state polymerization is the method of choice, providing higher or absolute polymerizability and selectivity arising from the anisotropic arrangement of monomer molecules in the crystal.

Toda *et al.* have revealed that lots of organic reactions take place in the solid state,[3] which suggest that potentially solid-state methods have wide applicability.[4] Thus far, solid-state polymerization[5] exists as a largely uncultivated area but has promising potential as a general methodology for polymer synthesis. This idea prompted us to start our project of developing new areas of solid-state polymerization.

Since a simple reaction is best for an initial study, we planned to apply a known solid-state reaction to a bifunctional compound for novel solid-state polycondensation.[6] Herein we have investigated the solid-state oxidative-coupling polymerization of 2,6-dihydroxynaphthalene (2,6-DHN) with $FeCl_3 \cdot 6H_2O$ (Scheme 1),[7] which is based on the report by Toda *et al.* concerning the effective production of 1,1′-bi-2-naphthol from 2-naphthol in the solid state.[8]

There are two reports dealing with the oxidative-coupling polymerization of 2,6-DHN.[9] One is about solution polymerization with $FeCl_3$, which, due to its poor solubility, yielded only the dimer to tetramer forms.[10] The other is about electrical oxidation, which produced the heptamer as well as larger oligomers.[11]



Scheme 1

We have found that grinding crystalline 2,6-DHN (or its amine-complex) with powdery $FeCl_3 \cdot 6H_2O$ using an agate pestle and mortar produces poly(2,6-dihydroxy-1,5-naphthylene), which was fully acetylated for characterization (Scheme 1 and Table 1).[12] In the first attempt (runs 1 and 2), 2,6-DHN was used as received (Aldrich). The oligomer was obtained by heating the mixture at 50 °C, while the reaction at rt produced a comparable oligomer, but only in low yield. The ^1H NMR spectrum of the acetylated polymer is informative to evaluate the degree of polymerization (Table 1); the acetyl protons located at the terminal (δ 2.46) are distinguishable from the internal ones (δ 1.91 and 2.02).[13] Purification of 2,6-DHN by recrystallization as well as sublimation did not result in improved polymerizability. Use of the more powerful oxidant, anhydrous $FeCl_3$, in place of $FeCl_3 \cdot 6H_2O$ induced further oxidation producing the quinone moiety, as indicated by the IR spectrum.

Therefore, it is essentially required to change the spatial arrangement of 2,6-DHN molecules in the crystal for efficient solid-state polymerization. For that purpose, we planned to use an amine to complex with 2,6-DHN through hydrogen bonding between the amine and the acidic hydroxy groups of 2,6-DHN. The molecular packing of 2,6-DHN in the co-crystal could then be varied using different amines. Several amine complexes were prepared by crystallization from an amine–2,6-DHN mixture in EtOAc or MeOH and these were then subjected to solid-state polymerization with $FeCl_3 \cdot 6H_2O$ (runs 3–10 in Table 1). The polymerization of amine complexes was found to take place more effectively, even at rt, than 2,6-DHN alone (run 2). The benzylamine complex was found to give the highest molecular weight polymer, and in good yield (run 6).

In order to clarify the higher polymerizability of 2,6-DHN in the benzylamine complex, X-ray crystallographic analysis was performed.[14] Fig. 1 shows 2,6-DHN and benzylamine molecules making alternating self-layers and 2,6-DHN molecules orienting horizontally in the layer, which seems to be preferable for the polymerization as compared with the reported crystal structure of 2,6-DHN.[15] The distance between the carbon atoms that will be connected to each other and the dihedral angle between two naphthalene ring planes are important for the reaction. However, the alternately layered structure of the benzylamine complex is probably essential to produce the higher polymer. The benzylamine layer prevents the interlayer reaction of 2,6-DHN so that the polymer chain should be extended in the horizontal direction within the 2,6-DHN layer. On the other hand, in the crystal of 2,6-DHN alone, the reaction can take place in random directions, resultantly, causing the growth of the polymer chains to be disturbed by each other.

Although the powder X-ray analysis indicated that the crystal structure is rapidly collapsed by mixing with $FeCl_3 \cdot H_2O$, the finding that the polymerizability is dependent on the amine suggests that it is the original crystal structure that determines polymerizability.

The amount of $FeCl_3 \cdot 6H_2O$ was reduced in run 10, since it was expected to work catalytically due to air-oxidation.

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† Electronic supplementary information (ESI) available: experimental procedures, ^1H, ^{13}C NMR and IR spectra of the acetylated polymer, crystal data of 2,6-DHN–benzylamine complex, and 3D graphics of the polymer models and of the crystal cells (2,6-DHN and its benzylamine complex). See http://www.rsc.org/suppdata/cc/b1/b107738d/

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Table 1 Oxidative-coupling polymerization of 2,6-DHN in the solid state[a]

Run	Amine[b] (DHN : amine)	Temp./ °C	Time (days)	Ac yield (%)[c]	M_w[d]	M_n[d]	M_w/M_n[d]	DP[e]	m : r[f]
1	None	50	1	83	5300	2800	1.8_9	4.7	
2	None	rt	3	15	4700	3200	1.4_8	7.9	
3	*rac*-DAC (1 : 1)	rt	1	47	7400	4000	1.8_3	9.2	
4	(*R*,*R*)-DAC (1 : 1)	rt	1	67	9500	4000	2.3_4	8.4	38 : 62
5	EDA (1 : 1)	rt	2	41	4900	3300	1.4_8	8.3	41 : 59
6	$BnNH_2$ (1 : 2)	rt	1	79	24500	9800	2.5_1	17.0	54 : 46
7	(*R*)-PEA (1 : 1)	rt	1	83	9600	5100	1.8_9	14.3	50 : 50
8	*m*-XyDA (1 : 1)	rt	1	42	8100	4600	1.7_7	9.6	43 : 57
9	*p*-XyDA (1 : 1)	rt	1	>99	5400	3600	1.5_0	9.1	37 : 63
10[g]	$BnNH_2$ (1 : 2)	rt	5	23	25700	8700	2.9_6	11.2	

[a] 2,6-DHN–$FeCl_3 \cdot 6H_2O$ = 1 : 3 except for run 10. 2,6-DHN was almost completely converted except for runs 2, 5, and 10. [b] *rac*-DAC: racemic *trans*-1,2-diaminocyclohexane, (*R*,*R*)-DAC: (1*R*,2*R*)-1,2-diaminocyclohexane, EDA: ethylenediamine, $BnNH_2$: benzylamine, (*R*)-PEA: (*R*)-α-phenylethylamine, *m*-XyDA: *m*-xylylenediamine, *p*-XyDA: *p*-xylylenediamine. [c] Yield of the acetylated polymer. [d] Measured by GPC in $CHCl_3$ (polystyrene standard). [e] Degree of polymerization, calculated from ^1H NMR spectrum ($CDCl_3$ or CF_3COOD), see text. [f] The ratio of *racemo* to *meso*, see text. [g] 2,6-DHN–$FeCl_3 \cdot 6H_2O$ = 1 : 1.

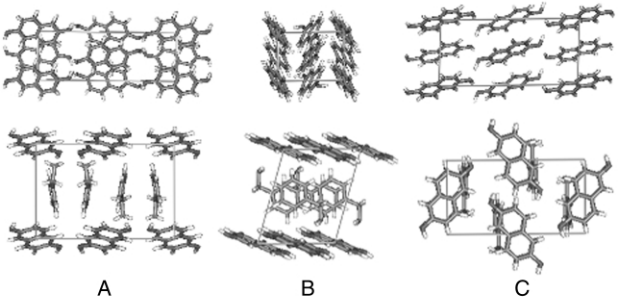

Fig. 1 The crystal structures of 2,6-DHN (upper) and 2,6-DHN–benzylamine 1 : 2 complex (lower). The views from three directions along a, b, and c axes are shown as A, B, and C, respectively.

Unfortunately, the reaction virtually stopped before the complete conversion of 2,6-DHN, giving the polymer in only low yield; its molecular weight, however, was comparable to that produced in run 6.

The product polymers have a kind of tacticity, which arises from atropisomerism due to the restricted rotation around the 1,1′-bond of the bi-2-naphthol moiety formed. The solid state polymerization would be expected to control the tacticity by ordered arrangement of the monomer molecules in the crystal. However, the product polymers were unfortunately found to be atactic (Table 1), as revealed by the ^1H NMR spectrum. The internal acetyl groups show two distinguishable peaks due to the diad; the peaks at δ 1.91 and 2.02 are ascribable to the *racemo* and *meso,* respectively.[16] The *meso–racemo* ratios shown in Table 1 were evaluated by integral proportion using a curve-fitting method.[17] Further study is ongoing in order to obtain the stereo-regular polymer.[18]

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5 Although it is necessary to consider the arguments in Ref. 4, we adopt herein the conventional term of solid-state polymerization. This term has been inclusively used for a system where a solid state is macroscopically preserved throughout polymerization.

6 In one of Toda′s reports, there is one brief example that a solid-state reaction of a bifunctional compound produced the linear oligomer: F. Toda and Y. Tokumaru, *Chem. Lett*., 1990, 987.

7 Our reasons for choosing this system as the first target come from our interests not only in the polymerization itself but also in the polymer produced. Solid-state polymerization must be preferable for the synthesis of a polymer having poor solubility. The prospective polymer, poly(2,6-dihydroxy-1,5-naphthylene), is an attractive material due to the rigid chain consisting of the bi-2-naphthol moiety, which can easily accept a variety of chemical modifications.

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12 The detailed procedures of the polymerization and the acetylation are available together with the ^1H, ^{13}C NMR and IR spectra of the acetylated polymer in the ESI.

13 The peak assignment is based on the model study in Ref. 11.

14 *Crystal data* for 2,6-DHN–benzylamine (1 : 2) complex: $C_{24}H_{26}N_2O_2$, M = 374.47, monoclinic, a = 7.6490(6), b = 13.7087(17), c = 9.7362(13) Å, β = 106.118(2)°, U = 980.79(19) Å^3, T = 173 K, space group $P2_1/a$, Z = 2, μ(Mo-Kα) = 0.081 mm^{-1}, 8037 reflections measured, 2232 unique (R_{int} = 0.0360) which were used in all calculations. Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0499, $wR2$ = 0.1195. CCDC 171458. See http://www.rsc.org/suppdata/cc/b1/b107738d/ for crystallographic data in .cif and other electronic formats.

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16 In ESI, the peak assignments are explained in the experimental document and shown with the ^1H NMR spectrum.

17 The detail of the evaluation is mentioned in the experimental document in ESI.

18 The stereo-regular polymers have attractive molecular shapes. See ESI for computer graphics of the isotactic and syndiotactic 12mer models.