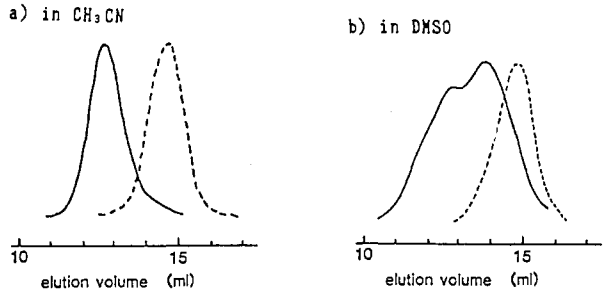

Figure 1. GPC curves of the polymer induced by the polymer initiator (—) and the starting polymer initiator (---).

diethyl malonate, to give adduct **4**. A nucleophilic site of **2** abstracts the methylene proton of diethyl malonate to generate malonate anion, which attacks the electrophilic site of **2** and the reductive elimination of Pd(0) takes place. Adduct **4** also has active protons, so that it continues to react with another π-allyl complex. Thus, the repetition of these elemental reactions gives rise to the production of polymer **3**.

As a support of the above mechanism of polymerization, it is worth mentioning that the isolated polymer **3** functioned as initiator; i.e., the isolated polymer **3** ($\bar{M}_n$ = 3300) (2 mol % for **1** based on the end groups) was stirred with the monomer **1** in CH_3CN, in the presence of a catalyst. After 24 h at room temperature, 88% **1** was consumed (GLC) and the polymer was obtained in 67% yield. A GPC curve of the produced polymer was found to be unimodal with a peak at a higher molecular weight region ($\bar{M}_n$ = 6300) (Figure 1a).

On the other hand, when the same reaction was carried out in DMSO, a GPC curve of the resultant polymer was bimodal (Figure 1b). This finding is explained assuming that the polymerization in DMSO was induced not only by the polymer initiator but also by a compound having an active proton which was probably derived by the isomerization of **1**.[11]

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Registry No. dppe, 1663-45-2; $Pd_2(dba)_3$, 51364-51-3; $CH_2(CO_2Et)_2$, 105-53-3; $BuNH_2$, 109-73-9; $CHCl_3$, 67-66-3; aniline, 62-53-3; diethyl 2-vinylcyclopropane-1,1-dicarboxylate, 7686-78-4.

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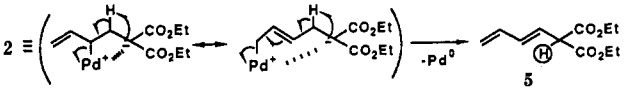
(7) This kind of synthetic reaction has been developed also in our laboratory: Tsuda, T.; Tokai, M.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 5216 and articles cited therein.
(8) Cho, I.; Ahn, K.-D. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3169.
(9) Inadequate purification of **1** causes the polymer yield to increase. A small amount of contaminant, which has an active proton, probably acts as an initiator.
(10) A methanol-soluble oligomer, whose main structure is the same as that of the methanol-insoluble polymer, is produced along with the unidentified side reaction product.
(11) A plausible isomerization of the monomer **1** is β-hydrogen elimination in intermediate **2**, generating diene **5**.



Masato Suzuki, Shuji Sawada, and Takeo Saegusa*
Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Kyoto 606, Japan

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Linear Poly(quinoxalones)

Linear poly(quinoxalines) represent an important family of high-temperature materials.[1] Poly(quinoxaline)[2] (PQ) and poly(phenylquinoxaline)[3] (PPQ) have been the most widely studied quinoxaline-based polymers and are generally prepared by the reaction of bis(*o*-diamines) with bis(glyoxals) and bis(benzils), respectively. In contrast, poly(quinoxalone) (PQO) has received much less attention relative to PQ and PPQ. The formation of PQOs can be envisaged to occur by step-growth polymerization of a bis(*o*-diamine) with a difunctional α-ketocarboxylic acid derivative. The only documented synthesis of PQO entailed polymerization of *p*-phenylenediglyoxalic acid with 3,3′-diaminobenzidine (DAB) in phenyl ether at the reflux temperature, followed by heating the "prepolymer" under vacuum from 200 to 350 °C.[4] The resulting PQO had good thermal stability and was soluble in sulfuric acid. The polymerization was beset with several problems, including difficulty in preparing *p*-phenylenediglyoxalic acid in high yield and purity and its decarbonylation under the polymerization conditions.

A reinvestigation of PQO was undertaken since certain aspects of the PQO structure may be manifested in distinct properties relative to PPQ and PQ. The reaction of methyl phenylglyoxalate with *o*-phenylenediamine was studied to determine the best conditions for selective quinoxalone formation (Scheme I). We chose to use *N*-methylpyrrolidone (NMP), a basic polar aprotic solvent, as the reaction solvent for the model study since it would likely be a good solvent for the polymerization.[5] When the reaction was carried out in NMP at 150 °C, formation of a multitude of products occurred. However, when the reaction was conducted at 60 °C in the presence of trifluoroacetic acid as a catalyst (5–10 mol %) a single product was formed. The product was isolated as an off-white crystalline solid and was identified as the desired 3-phenylquinoxalone (**1**) (mp = 251–252 °C (lit.[6] 250–252 °C)). Other effective catalysts included *p*-toluenesulfonic acid, acetic acid, concentrated hydrochloric acid, and boron trifluoride etherate. Exclusive formation of **1** also occurred when methanesulfonic acid was substituted for NMP as the reaction solvent. The model study showed that the acid-catalyzed condensation of *o*-diamines and α-keto esters affords quinoxalones in both high yield and selectivity, indicative of a good polymer-forming reaction. By use of acid catalysis, the desired quinoxalone product is formed at temperatures well below the decarbonylation temperature of the α-keto ester monomer, eliminating this potential side reaction.

A single-step preparation of the bis(α-keto ester) monomer was achieved using a Friedel–Crafts acylation of

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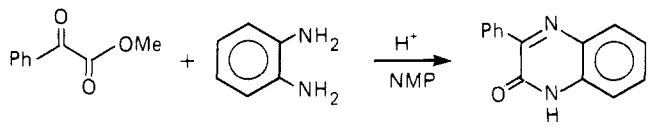
Scheme I



1

activated aromatic substrates with methyl oxalyl chloride as the electrophile.[6] Dimethyl 2,2′-oxybis-*p*-phenylenediglyoxalate (**2**) was synthesized by slowly adding 46.6 g (0.38 mol) of methyl oxalyl chloride to 25.0 g (0.147 mol) of diphenyl ether and 85 g (0.64 mol) of aluminum chloride in 250 mL of methylene chloride at 0 °C. Upon completion of the methyl oxalyl chloride addition, the reaction mixture was treated with an additional 150 mL of methylene chloride, stirred 1 h at 0 °C, and allowed to warm to room temperature overnight. The aluminate complex was isolated by filtration, washed with methylene chloride, and added to 400 mL of 50% aqueous hydrochloric acid slurried with crushed ice. The crude product was isolated and recrystallized (methanol) to afford 25 g (50%) of **2** as a white crystalline compound.[7] This method should be applicable to analogous substrates which are active toward disubstitution in Friedel–Crafts reactions, e.g., diphenyl sulfide.[8]

Initial attempts to synthesize PQOs were conducted by dissolving equimolar amounts of **2** and a tetramine in NMP (≃12% solids), followed by the addition of 10 mol % trifluoroacetic acid. The resulting solution was heated to 60 °C for 16–24 h to effect the polymerization (Scheme II). When the polymerization was carried out by heating **2** and 3,3′-diaminobenzidine (DAB) for 16 h at 60 °C, a mixture comprised of a fine precipitate suspended in a viscous polymer solution was obtained after 16 h. Tough, clear films could be prepared from the polymerization mixture, with no visible sign of the particles that were present in the polymerization dope. Separation of the precipitate was effected by diluting the polymerization mixture followed by centrifugation. The yellow precipitate was isolated by filtration and washed with NMP and was found to constitute less than 5 wt % of the total material isolated. The soluble polymer, I, was isolated as a yellow fibrous material by precipitation in methanol. IR spectra of both the precipitate and the soluble polymer displayed the characteristic quinoxalone carbonyl band at 1660 cm^{-1}, indicative of poly(quinoxalone) formation. Coagulation of the polymer in methanol without separating the precipitate resulted in a material that was fully soluble in methanesulfonic acid, as well as a 5% solution of lithium chloride in NMP at 50 °C. Attempts to prepare I in an NMP/5% LiCl solvent mixture did not afford high polymer, presumably due to a side reaction involving the chloride ion.[9] Polymerization of **2** with 3,3′,4,4′-tetraaminodiphenyl ether (TADE) went smoothly to afford a fully soluble, high molecular weight PQO, II (entry 1, Table I). Polymerization of **2** with 3,3′,4,4′-tetraaminobenzophenone (TAB) under these conditions resulted in gel formation, presumably due to cross-linking through the carbonyl group of TAB. Thus, the preparation of PQOs in NMP can be problematic but appears to be suitable for more flexible PQO structures, e.g., II.

Table I
Synthesis of Poly(quinoxalones)

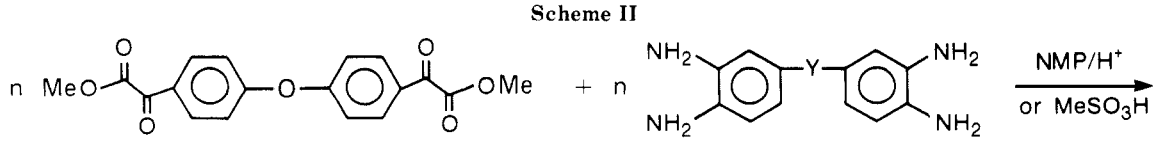
entry	polymer	polymn solvent	2:amine	$[\eta]$,[a] dL/g
1	II	NMP	0.99	1.15
2	I	MSA[b]	1.01	0.83
3	II	MSA	0.99	0.63
4	III	MSA	1.01	1.29

[a] NMP, 20 °C. [b] MSA = methanesulfonic acid.

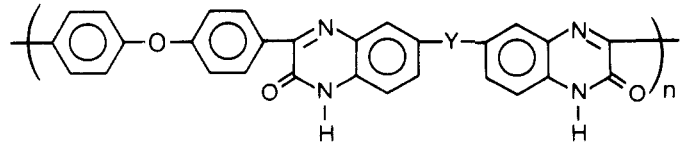
A more general method for preparing PQOs involved using methanesulfonic acid as the polymerization solvent. Polymerization of **2** with DAB, TADE, and TAB was carried out by dissolving the tetramine in methanesulfonic acid, followed by addition of **2** to the solution and heating at 60 °C for 16–24 h, affording viscous deep-red solutions. Polymers I–III were isolated by precipitation in 10% aqueous base and washed with a 5% potassium carbonate solution, water, and dilute acetic acid to effect removal of the methanesulfonic acid. High molecular weight PQOs were obtained by this procedure, as indicated by the intrinsic viscosity measurements (entries 2–4, Table I). The PQOs were fully soluble in NMP and, surprisingly, were insoluble in *m*-cresol and chlorinated solvents, both of which are good solvents for PPQ. The reason PQOs prepared in methanesulfonic acid are fully soluble in NMP may be related to the constitutional isomer mix in the polymer backbone.[10] Tough, fingernail-creasable films were obtained from NMP solutions when heated to remove solvent. It was found advantageous to offset the stoichiometry slightly to obtain more processable materials. The IR spectra of I prepared in both NMP and methanesulfonic acid were found to be identical, both showing the characteristic quinoxalone carbonyl band at 1660 cm^{-1} (Figure 1).

The thermal and mechanical properties of the PQOs were exceptionally good. Dynamic TGA measurements on I showed polymer decomposition temperatures (5% weight loss) of 510 °C in nitrogen and 480 °C in air. The iso-

Scheme II



2



I: Y = nil
II: Y = O
III: Y = C=O

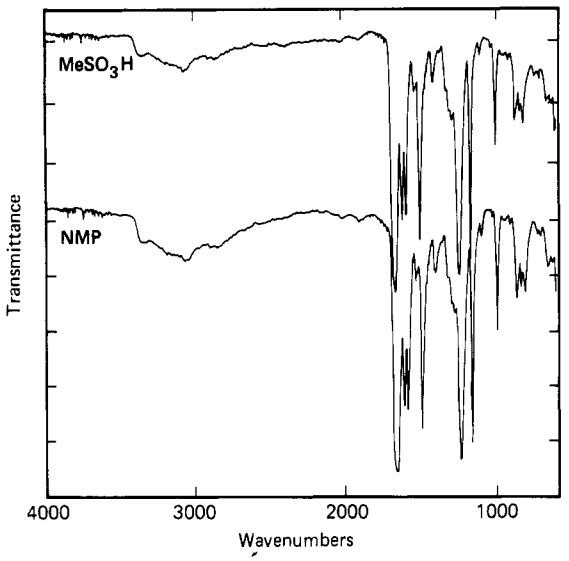


Figure 1. Infrared spectra of polymer I prepared in both NMP and methanesulfonic acid.

Table II
PQO Thermal and Mechanical Properties

polymer	T_g, °C	modulus, MPa	stress at break, MPa	elongation, %
I	>450	4000	160	15
II	375	3300	135	18
III	410			
PPQ[a]	340	2700	130	10

[a] Derived from 1,4-bis(phenylglyoxalyl)benzene and DAB.

thermal weight loss of a film of I was 0.06 wt %/h at 400 °C in nitrogen and 0.70 wt %/h at 250 °C in air (12-h heating period). These values demonstrate that the thermal stability of I is excellent, comparable to aromatic polyimides, though slightly lower than PPQ. The thermal stability of III was comparable to I, while II was lower with a polymer decomposition temperature of 460 °C in nitrogen. The dimensional stability of these materials was outstanding as determined by both differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) (Table II). The glass transition temperature (T_g) of I, prepared by either route, was not detectable by DSC up to 450 °C. T_g's of 375 and 410 °C were observed for II and III, respectively. The DMTA of I showed no drop in the modulus or damping peak in the tan δ curve up to 450 °C. These values represent exceptionally high transition temperatures for amorphous polymers containing ether and carbonyl linkages. Indeed, the analogous ether- and carbonyl-containing PQ and PPQ materials display T_g's ranging from 240 to 280 °C.[1,11-12] Mechanical property measurements (ambient temperature) showed I and II to be ductile, high modulus materials and are compared to PPQ in Table II.

In summary, a new monomer synthesis and milder polymerization conditions compatible with α-keto esters have been developed for the preparation of high molecular weight linear PQOs from bis(α-keto esters) and bis(*o*-diamines). The polymers are NMP soluble as fully cyclized structures, precluding the need for high-temperature curing. Moreover, as NMP is a commonly used solvent for polymer processing in microelectronics applications, PQO could offer a significant advantage to other poly(quinoxalines) for applications in the electronics industry, as well as other areas requiring new high-performance polymers. The materials displayed excellent dimensional and thermal stability, as well as tough, ductile mechanical properties. This represents an exceptional combination of properties, portending interesting structure–property relationships. It can be speculated that the predominance of one constitutional isomer in the polymer backbone, due to the greater reactivity of the ketone carbonyl relative to the ester,[10] and hydrogen bonding associated with the amide moiety of the quinoxalone ring plays a significant role in the properties of these materials.

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Registry No. 1, 1504-78-5; **2**, 118771-46-3; I (copolymer), 118771-47-4; I (SRU), 118892-33-4; II (copolymer), 118771-49-6; II (SRU), 118892-34-5; III (copolymer), 118771-48-5; III (SRU), 118920-15-3; NMP, 872-50-4; methyl phenylglyoxalate, 15206-55-0; *o*-phenylenediamine, 95-54-5; trifluoroacetic acid, 76-05-1; methyloxalyl chloride, 5781-53-3; diphenyl ether, 101-84-8; aluminum chloride, 7446-70-0; methanesulfonic acid, 75-75-2.

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(5) The quinoxalone model compounds previously prepared were soluble in aqueous base (ref 4), presumably due to the formation of the sodium salt of the hydroxyquinoxaline tautomer of the quinoxalone. We thought basic aprotic solvents would prove to be good solvents for PQO due to the potential for specific interaction of the solvent with the quinoxalone ring.
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(7) The characteristic physical and spectral properties of **2** are as follows: mp = 96–97 °C; IR (KBr) 2958, 1737 (ester C=O), 1685 (ketone C=O), 1161 (C—O) cm^{-1}; H NMR ($CHCl_3$) δ (ppm) 4.0 (s, 6 H), 7.1 (d, 4 H, J = 10 Hz), 8.1 (d, 4 H, J = 10 Hz). Anal. Calcd for $C_{12}H_{10}O_6$: C, 63.16; H, 4.12. Found: C, 63.00; H, 4.08.
(8) Since submission of the original manuscript, dimethyl 2,2′-thiobis-*p*-phenylenediglyoxalate has been synthesized in high yield by this procedure using a methylene chloride/carbon disulfide solvent mixture.
(9) The reaction of methyl phenylglyoxalate and 1,2-phenylenediamine was carried out in NMP/5% LiCl at 60 °C. HPLC analysis showed 1 was not formed selectively, and a unidentified side product was present. The side product formation may involve nucleophilic addition of the chloride ion to a reaction intermediate.
(10) Model reactions of *p*-anisidine with methyl phenylglyoxalate in NMP gave a single product which was identified as the imino ester adduct. This demonstrates that selective addition to the ketone carbonyl will occur in the polymerization and that, depending on the tetramine, one constitutional isomer should be formed predominantly in the polymer backbone, analogous to PQs (ref 2c). The polymerization in methanesulfonic acid may not be as selective, which would lead to a greater degree of constitutional isomerism, affording a material with improved solubility.
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Jeff W. Labadie

IBM Research, Almaden Research Center
650 Harry Road, San Jose, California 95120

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