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Synthesis of Aromatic Poly(ether ketones)

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ABSTRACT: A convenient method for the synthesis of certain aromatic poly(ether ketones) of high molecular weights has been developed. These polymers were prepared readily by direct polycondensation of dicarboxylic acids containing phenyl ether structures with diphenoxybenzene or by self-polycondensation of phenoxybenzoic acid using phosphorus pentoxide/methanesulfonic acid (PPMA) as condensing agent and solvent. Polycondensations proceeded smoothly and produced aromatic poly(ether ketones) with inherent viscosities up to 1.5 dL·g^{-1}. The synthesis of substituted diaryl ketones by the reaction of aromatic carboxylic acids or dicarboxylic acids with methoxybenzene in PPMA was studied in detail to demonstrate the feasibility of the reaction for polymer formation. The thermogravimetry of the aromatic poly(ether ketones) showed 10% weight loss in air and nitrogen at around 460 and 490 °C, respectively.

Introduction

Since poly(phenylene ether ketone) (PEEK) has shown promise as an excellent engineering plastic because of its good mechanical property and thermooxidative stability, the synthesis of aromatic poly(ether ketones) has become of interest in recent years.

A number of synthetic routes for producing poly(ether ketones) have been described in the literature.[1] They can be prepared in two ways, by a nucleophilic substitution reaction or an electrophilic reaction (Friedel–Crafts reaction) (eq 1). PEEK has been prepared by the latter method.

$$X\text{-}p\text{-}C_6H_4C({=}O)\text{-}p\text{-}C_6H_4X + M^{+-}OArO^{-}M^{+} \rightarrow -(O\text{-}p\text{-}C_6H_4C({=}O)\text{-}p\text{-}C_6H_4OAr)_n- \quad (1)$$

$$XC({=}O)ArC({=}O)X + C_6H_5OC_6H_5 \rightarrow -(p\text{-}C_6H_4O\text{-}p\text{-}C_6H_4C({=}O)ArC({=}O))_n-$$

In preceding papers,[2,3] we showed that phosphorus pentoxide/methanesulfonic acid (PPMA) in a weight ratio of 1:10 as a substitute for poly(phosphoric acid) (PPA) is a very useful dehydrating agent for the preparation of aliphatic dicarboxylic acids with diaryl compounds. In order to expand the preparative utility of this method, it was applied to the synthesis of aromatic poly(ether ketones).

This article describes a successful synthesis of aromatic poly(ether ketones) by direct polycondensation of aromatic dicarboxylic acids containing phenyl ether structures with diphenoxybenzene or by self-polycondensation of phenoxybenzoic acid in PPMA.

Experimental Section

Materials. The reagent PPMA was prepared according to the reported procedure.[4] Various reagent grade substituted benzoic acids (**1**) and methoxybenzene (**2**) were used as received.

1,4-Diphenoxybenzene (**7b**) was prepared by the reaction of phenol with 1,4-dibromobenzene in the presence of copper. Recrystallization from ethanol yielded white plates, mp 78–79 °C (lit.[5] 77 °C).

4,4′-Oxydibenzoic acid (**4b**), 3,3′-(*p*-phenylenedioxy)dibenzoic acid (**4c**), 4,4′-(*p*-phenylenedioxy)dibenzoic acid (**4d**), 3-phenoxybenzoic acid (**11a**), and 4-phenoxybenzoic acid (**11b**) were prepared through oxidation of the corresponding methyl compounds with potassium permanganate in pyridine–water. These carboxylic acids were purified by recrystallization: **4b**, mp 337 °C (by DTA) (lit.[6] 331–333 °C from acetic acid); **4c**, mp 312 °C (by DTA) (lit.[7] 305–313 °C from acetic acid); **4d**, mp 333 °C (by DTA) (lit.[7] 331–333 °C from dioxane); **11a**, mp 151.5–152.5 °C (lit.[8] 145 °C from ethanol–water); (**11b**: mp 167–168 °C (lit.[9] 160 °C from methanol).

Substituted 4-Methoxybenzophenone (3). General Procedure. A mixture of substituted benzoic acid (**1**) (2.5 mmol) and methoxybenzene (**2**) (2.5 mmol) in the reagent (5 mL) was stirred at room temperature for several hours. The solution was poured into water and neutralized with sodium carbonate. The product was filtered, washed with water, and dried. The products were identified as the desired products by means of IR, ^{1}NMR spectra, and melting points.

1,3-Bis(4-methoxybenzoyl)benzene (5). A solution of isophthalic acid (**4a**) (0.166 g, 1.0 mmol) and **2** (0.216 g, 2.0 mmol) was stirred in PPMA (5 mL) at 60 °C for 15 min. The product was isolated as described above. The yield containing isomers was 0.364 g (99%). Recrystallization from ethanol gave white needles: mp 149–151 °C; IR (KBr) 1640 (C═O), 1240, 1020 cm^{-1} (C—O—C). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.70; H, 5.24. Found: C, 76.1; H, 5.3.

Oxybis[4-(4-methoxybenzoyl)benzene] (6). This compound was prepared from 4,4′-oxydibenzoic acid (**4b**) and **2**. The yield was 0.438 g (99%). Recrystallization from dioxane yielded white crystals: mp 245.5–246.5 °C; IR (KBr) 1630 (C═O), 1240, 1020 cm^{-1} (C—O—C). Anal. Calcd for $C_{28}H_{22}O_5$: C, 76.70; H, 5.06. Found: C, 76.5; H, 5.2.

(*p*-Phenylenedioxy)bis(4-benzoylbenzene) (9b). The yield was 99%. Recrystallization from acetone gas white plates: mp 199.5–200.5 °C; IR (KBr) 1640 (C═O), 1240 cm^{-1} (C—O—C). Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.67; H, 4.71. Found: C, 81.6; H, 4.7.

Polymer Synthesis: Two typical examples of the polymerization follow.

Polymer 10b from 4b and 7b. A solution of dicarboxylic acid **4b** (0.258 g, 1.0 mmol) and 1,4-diphenoxybenzene **7b** (0.262 g, 1.0 mmol) in PPMA (3 mL) was stirred at 120 °C for 10 h. The resulting viscous solution was diluted with methanesulfonic acid. This solution was poured into water (500 mL) and neutralized with sodium carbonate. The polymer was collected, washed with water, and refluxed in water for 2 h. The polymer was dried in vacuo at 80 °C for 2 days. The yield was 0.485 g (99%). The inherent viscosity of the polymer in concentrated sulfuric acid was 1.5 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. The IR (KBr) spectrum exhibited absorptions at 1650 (C═O) and 1220 cm^{-1} (C—O—C). Anal. Calcd for $(C_{32}H_{20}O_5{\cdot}{}^1/_2H_2O)_n$: C, 77.88; H, 4.29. Found: C, 77.27; H, 4.55.

Polymer 12a from 11a. Polymer **12a** was prepared from **11a** at 100 °C for 24 h as described above. The polymer, obtained in quantitative yield, has the inherent viscosity of 1.0 dL·g^{-1} in concentrated sulfuric acid (0.5 g·dL^{-1}) at 30 °C. The IR (film) spectrum showed absorptions at 1650 (C═O) and 1230 cm^{-1} (C—O—C). Anal. Calcd for $(C_{13}H_8O_2)_n$: C, 79.58; H, 4.11. Found: C, 78.64; H, 4.61.

Results and Discussion

Model Reaction. As described in the previous papers,[2,3] we succeeded in the synthesis of aliphatic poly(ether ketones) but failed in the synthesis of aromatic poly(ether

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Table I
Condensation of Benzoic Acid 1a with Methoxybenzene 2 in PPMA[a]

reactn conditns			reactn conditns		
amt of PPMA, mL	time, h	prod yield, %	amt of PPMA, mL	time, h	prod yield, %
3	1	60	5	2	85
3	3	86	5	3	92
5	1	66			

[a] Reaction was carried out with 2.5 mmol of each reactant at 20 °C.

Table II
Preparation of Methoxyphenylaryl Ketones 3 in PPMA[a]

				isomer distrib, %	
	RC_6H_5COOH	time, h	prod (yield, %)	para	ortho
1a		3	**3a** (92)	100	0
1b	p-CH_3	3	**3b** (95)	100	0
1c	o-CH_3O	8	**3c** (93)	100	0
1d	p-CH_3O	3	**3d** (97)	100	0
1e	o-Cl	3	**3e** (95)	90	10
1f	p-Cl	10	**3f** (96)	90	10
1g	p-NO_2	24	**3g** (79)	80	20

[a] Reaction was carried out with 2.5 mmol of each reactant in 5 mL of PPMA at 20 °C.

Table III
Preparation of Diketones in PPMA[a]

	reactn conditns			isomer distributn, %	
dicarboxylic acid	time, h	temp, °C	prod (yield, %)	p-p	p-o- + o-o-
4a	12	20	**5** (53)	70–85	15–30
4a	24	20	**5** (93)	70–85	15–30
4a	1	60	**5** (80)	70–85	15–30
4a	3	60	**5** (99)	70–85	15–30
4b	12	20	**6** (34)	100	0
4b	24	20	**6** (55)	100	0
4b	0.5	60	**6** (99)	100	0

[a] Reaction was carried out with 1 mmol of dicarboxylic acid and 2 mmol of methoxybenzene in 5 mL of PPMA.

ketones). Therefore, the reaction of benzoic acid (**1a**) with methoxybenzene (**2**) was studied in PPMA (eq 2). The

$$\underset{\mathbf{1}}{RC_6H_4C(=O)OH} + \underset{\mathbf{2}}{C_6H_5OCH_3} \rightarrow \underset{\mathbf{3}}{RC_6H_4C(=O)\text{-}p\text{-}C_6H_4OCH_3} \quad (2)$$

R: **a**, H; **b**, p-CH_3; **c**, o-CH_3O; **d**, p-CH_3O; **e**, o-Cl; **f**, p-Cl; **g**, p-NO_2

results are shown in Table I. The reaction proceeded at room temperature and gave 4-methoxybenzophenone (**3a**) quantitatively after 3 h. 5 mL of PPMA was found to be enough for the reaction on a 2.5-mmol scale based on **2**. The exclusive para position of the benzoyl group was revealed by means of NMR spectroscopy.

On the basis of these preliminary experiments, the reaction of substituted benzoic acids **1** with **2** was carried out at room temperature in PPMA. The data summarized in Table II indicate that the reagent PPMA acts both as a very strong condensing agent and solvent and gave good yields of the desired ketones under mild conditions. The compound **2** was easily acylated by benzoic acid containing electron-donating groups and produced exclusively the para products. On the other hand, benzoic acids with electron-withdrawing groups reacted slowly with **2** and gave the mixture of ortho and para isomers. These observations suggest that primary formation of mixed anhydride is assumed, which then dissociates into acylium ions under the influence of methanesulfonic acid.

Table IV
Preparation of Diketones in PPMA[a]

	reactn conditns				reactn conditns		
aryl ether	time, h	temp, °C	prod (yield, %)	aryl ether	time, h	temp, °C	prod (yield, %)
7a	24	20	**8a** + **9a**	**7b**	2	20	**8b** + **9b**
7a	6	60	**9a** (95)	**7b**	5	20	**9b** (99)

[a] Reaction was carried out with 1 mmol of aryl ether and 2 mmol of benzoic acid in 5 mL of PPMA.

Next, bifunctional model compound work was performed to determine if the desired model compounds were formed in quantitative yields to constitute a polymer-forming reaction.

First, the reaction of isophthalic acid (**4a**) or 4,4′-oxydibenzoic acid (**4b**) with **2** was studied (eq 3) (Table III).

$$\underset{\mathbf{4a}}{HOC(=O)\text{-}m\text{-}C_6H_4C(=O)OH} + \underset{\mathbf{2}}{2C_6H_5OCH_3} \rightarrow \underset{\mathbf{5}}{CH_3O\text{-}p\text{-}C_6H_4C(=O)\text{-}m\text{-}C_6H_4C(=O)\text{-}p\text{-}C_6H_4OCH_3}$$

$$\underset{\mathbf{4b}}{HOC(=O)\text{-}p\text{-}C_6H_4O\text{-}p\text{-}C_6H_4C(=O)OH} + \underset{\mathbf{2}}{2C_6H_5OCH_3} \rightarrow \underset{\mathbf{6}}{CH_3O\text{-}p\text{-}C_6H_4C(=O)\text{-}p\text{-}C_6H_4O\text{-}p\text{-}C_6H_4C(=O)\text{-}p\text{-}C_6H_4OCH_3} \quad (3)$$

The former reaction gave acylated compounds containing several isomers, although the yield was quantitative. Meanwhile, the latter reaction was slow at room temperature because of low solubility of **4b** in PPMA, but **4b** reacted rapidly with **2** at 60 °C. The reaction was almost complete within 30 min, affording quantitative yield of the para isomer.

Second, the reaction of **1a** with diphenyl ether (**7a**) or 1,4-diphenoxybenzene (**7b**) was conducted in PPMA in order to determine the structural effects in the aryl ether (eq 4). As shown in Table IV, the desired dibenzoyl

$$\underset{\mathbf{7}}{R} + \underset{\mathbf{1a}}{2C_6H_5C(=O)OH} \rightarrow \underset{\mathbf{8}}{RC(=O)C_6H_5} + \underset{\mathbf{9}}{C_6H_5C(=O)RC(=O)C_6H_5} \quad (4)$$

R: **a**, $C_6H_5OC_6H_5$; **b**, $C_6H_5O\text{-}p\text{-}C_6H_4OC_6H_5$

compound **9b** from **7b** was obtained in quantitative yield at room temperature. Meanwhile, dibenzoylation of **7a** took place slowly and required heating to complete the reaction because the benzoyl group in **8a** deactivates the other phenyl ring to electrophilic substitution.

Polymer Synthesis. In order to determine the optimal conditions for the polycondensation, the polycondensation of **4b** with 1,4-diphenoxybenzene (**7b**) was studied. The polycondensation was performed with 1 mmol of each monomer at 100 °C for 24 h. Table V lists the effect of the amount of PPMA on the polycondensation. Three mililiters of PPMA was found to be adequate for the reaction on a 1-mmol scale.

The effect of the reaction temperature on the inherent viscosity of the resulting polymer was examined over the temperature range 80–140 °C. The polycondensation at 120 °C gave polymer with an inherent viscosity as high as 1.5 $dL{\cdot}g^{-1}$ in 10 h. The polycondensation proceeded with the formation of a clear red solution at a temperature lower

Table V
Effect of Amount of PPMA on Polycondensation[a]

amt of PPMA, mL	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]	amt of PPMA, mL	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]
1	95	0.17	4	99	1.1
2	99	1.1	5	99	0.44
3	99	1.5			

[a] Polycondensation was carried out with 1 mmol of each monomer at 100 °C for 24 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

Table VI
Effect of Reaction Temperature on Polycondensation[a]

reactn temp, °C	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]	reactn temp, °C	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]
80	99	0.57	120	99	1.5
100	99	0.60	140	99	0.23

[a] Polycondensation was carried out with 1 mmol of each monomer in 3 mL of PPMA for 10 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

than 120 °C, but over 140 °C the solution became brown, probably because of some decomposition of monomer. These results are summarized in Table VI.

On the basis of these studies, direct polycondensation of aromatic dicarboxylic acids **4b**, 3,3′-(*p*-phenylenedioxy)dibenzoic acid (**4c**), and 4,4′-(*p*-phenylenedioxy)dibenzoic acid (**4d**) with **7b** was carried out at 120 °C in PPMA (eq 5). The results are listed in Table VII. The

$$\underset{\mathbf{4}}{\mathrm{HOC({=}O)RC({=}O)OH}} + \underset{\mathbf{7b}}{\mathrm{C_6H_5O\text{-}}p\text{-}\mathrm{C_6H_4OC_6H_5}} \rightarrow \underset{\mathbf{10}}{-(\mathrm{C({=}O)RC({=}O)\text{-}}p\text{-}\mathrm{C_6H_4O\text{-}}p\text{-}\mathrm{C_6H_4O\text{-}}p\text{-}\mathrm{C_6H_4})_n{}^{N}} \qquad (5)$$

R: **b**, p-C_6H_4O-p-C_6H_4; **c**, m-C_6H_4O-p-C_6H_4O-m-C_6H_4;
d, p-C_6H_4O-p-C_6H_4-O-p-C_6H_4

polycondensation of **4a** or **4b** proceeded in homogeneous solution and gave quantitative yields of polymer **10** with high molecular weights. On the other hand, the polycondensation of **4d** in PPMA proceeded along with polymer precipitation, which yielded limited molecular weights.

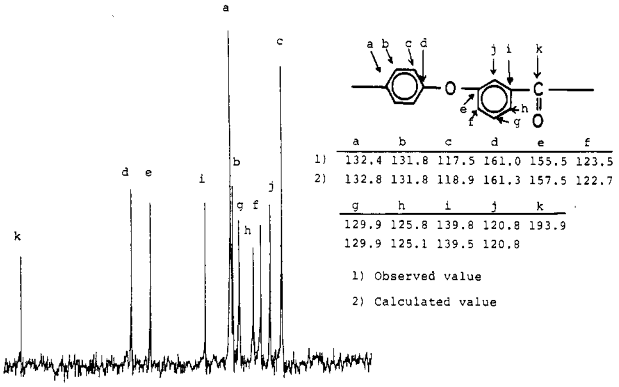
Next, the synthesis of poly(ether ketones) by direct self-polycondensation of phenoxybenzoic acid (**11**) was performed under conditions similar to those described for the preparation of polymer **10** (eq 6). Table VIII indicates

$$\underset{\mathbf{11}}{\mathrm{RC({=}O)OH}} \rightarrow \underset{\mathbf{12}}{-(\mathrm{RC({=}O)})_n-} \qquad (6)$$

R: **a**, C_6H_5O-m-C_6H_4; **b**, p-C_6H_5O-p-C_6H_4

that poly(ether ketone) **12a** from 3-phenoxybenzoic acid (**11a**) was easily produced in quantitative yield with inherent viscosities up to 1.0 dL·g^{-1} at 100 °C for 24 h. Only low molecular weight polymer from 4-phenoxybenzoic acid (**11b**) was obtained under various conditions because of the precipitation of the resulting polymer **12b** and lower electrophilicity of **11b** than **11a** due to the presence of the deactivating group at the para position. Furthermore, the decarboxylation of **11b** was observed at 140 °C. The decarboxylation of aromatic carboxylic acids in a strong acid, which is known to take place, generally is accelerated by the presence of electron-donating groups on the ortho and para positions.

Polymer Characterization. The polymers were defined as poly(ether ketones) by comparing their IR spectra with those of model compounds. The IR spectra exhibited characteristic absorptions at around 1640 and 1240 cm^{-1} due to the C=O and C—O—C stretching. Elemental analyses also supported the formation of the expected polymers.



	a	b	c	d	e	f
1)	132.4	131.8	117.5	161.0	155.5	123.5
2)	132.8	131.8	118.9	161.3	157.5	122.7

	g	h	i	j	k
1)	129.9	125.8	139.8	120.8	193.9
2)	129.9	125.1	139.5	120.8	

1) Observed value
2) Calculated value

Figure 1. ^{13}C NMR spectrum of polymer **12a**.

Table VII
Preparation of Aromatic Poly(ether ketones) 10 in PPMA[a]

dicarboxylic acid	reactn conditns amt of PPMA, mL	reactn conditns time, h	polymer	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]
4b	3	10	**10b**	99	1.5
4c	3	2.5	**10c**	99	0.81
4c	3	3	**10c**	99	1.4[c]
4d	3	24	**10d**	99	0.26
4d	4	24	**10d**	99	0.20

[a] Polycondensation was carried out with 1 mmol of each monomer in PPMA at 120 °C. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. [c] Measured at a concentration of 0.5 g·dL^{-1} in methanesulfonic acid at 30 °C.

Table VIII
Preparation of Aromatic Poly(ether ketones) 12 in PPMA[a]

carboxylic acid	reactn conditns amt of PPMA, mL	reactn conditns temp, °C	polymer	polymer yield, %	polymer η_{inh}, dL·g^{-1} [b]
11a	2	80	**12a**	99	0.65
11a	1	100	**12a**	99	0.11
11a	2	100	**12a**	99	1.0
11a	3	100	**12a**	99	0.43
11a	2	120	**12a**	99	0.69
11a	2	140	**12a**	99	0.13
11b	2	100	**12b**	99	0.15
11b	4	100	**12b**	99	0.32
11b	4	120	**12b**	99	0.18
11b	4	140	**12b**	dec	dec
11b	6	100	**12b**	99	0.27

[a] Polycondensation was carried out with 2.5 mmol of the monomer for 24 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C.

The most conclusive spectral evidence for the proposed poly(ether ketone) structures, and especially for the selective para acylation rather than ortho acyl formation, was provided by ^{13}C NMR. The typical ^{13}C NMR spectrum of polymer **12a** is shown in Figure 1 together with assignments of the observed resonances. The calculated chemical shifts are all within ±1 ppm of observed values. No duplication of peaks was found, clearly indicating formation of para acylated linkages during polymerization.

The poly(ether ketones) were white to brown solids. The polymer **10b** was soluble only in concentrated sulfuric acid and methanesulfonic acid. In contrast, polymers **10c** and **12a** were soluble both in strong acids and in polar aprotic

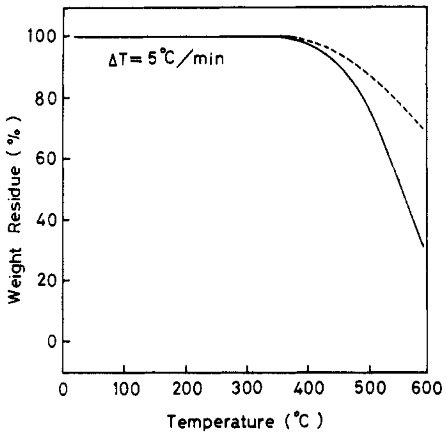


Figure 2. TG curves of polymer **10b**: (—) in air; (- - -) in nitrogen.

Table IX
Thermal Properties of Poly(ether ketones)

			decomp temp, °C[a]	
polymer	T_g, °C	T_m, °C	in air	in nitrogen
10b	165	352	455	485
10c	147	350	465	480
12a	133		485	510

[a] Temperature at which a 10% weight loss was recorded by TG at a heating rate at 5 °C·min^{-1}.

solvents. In particular, polymer **12a** was soluble in haloalkanes. Film, cast from the solution of polymer **12a** in dichloromethane, shows a high degree of toughness.

The thermal stability of polymers was examined by thermogravimetry (TG). A typical trace for polymer **10b** is shown in Figure 2. The polymer showed a 10% weight loss at 455 °C in air. Differential scanning calorimetry on powders showed weak but reproducible endotherms at 165 and 352 °C, which reflected the glass transition temperature and melting point, respectively. These data are presented in Table IX.

In conclusion, we showed poly(ether ketones) with high molecular weights are prepared by direct polycondensation of dicarboxylic acids **4** containing phenyl ether structures with **7b** or self-polycondensation of 3-phenoxybenzoic acid (**11a**) in PPMA as both a condensing agent and solvent. This method is advantageous for the formation of poly(ether ketones) because of its simplicity compared to conventional methods. The disadvantage of this method is that typical dicarboxylic acids, such as isophthalic acid and terephthalic acid, cannot be used.

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Registry No. **1a**, 65-85-0; **1b**, 99-94-5; **1c**, 579-75-9; **1d**, 100-09-4; **1e**, 118-91-2; **1f**, 74-11-3; **1g**, 62-23-7; **2**, 100-66-3; **3a**, 611-94-9; **3b**, 23886-71-7; **3c**, 5449-69-4; **3d**, 90-96-0; **3e**, 54118-74-0; **3f**, 10547-60-1; **3g**, 1151-94-6; **4a**, 121-91-5; **4b**, 2215-89-6; **5**, 7477-29-4; **6**, 110418-37-6; **7a**, 101-84-8; **7b**, 3061-36-7; **9a**, 6966-89-8; **9b**, 104017-40-5; **10b** (copolymer), 88049-80-3; **10b** (SRU), 60015-04-5; **10c** (copolymer), 110418-43-4; **10c** (SRU), 110418-46-7; **10d** (copolymer), 88049-83-6; **10d** (SRU), 110418-47-8; **11a** (homopolymer), 27938-17-6; **11b** (homopolymer), 27938-16-5; **12a**, 110418-45-6; **12b**, 27380-27-4; P_2O_5, 1314-56-3; H_3CSO_3H, 75-75-2.

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