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Shizunobu Hashimoto[a]; Isao Furukawa[a]; Keiji Ueyama[a]
[a] Department of Applied Chemistry Doshisha, University Kamigyo, Kyoto, Japan

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Synthesis and Properties of Phosphorus-Containing Aromatic Polyethers

SHIZUNOBU HASHIMOTO, ISAO FURUKAWA, and KEIJI UEYAMA

Department of Applied Chemistry
Doshisha University
Kamigyo, Kyoto 602, Japan

ABSTRACT

The phosphorus-containing aromatic polyethers were prepared from bis(p-chlorophenyl)phenylphosphine oxide (BCPO) with the sodium salt of several bisphenols by high temperature solution polycondensation. The best result (yield 84%, $\eta_{sp}/c = 0.15$) was obtained from BCPO with bisphenol A (BPA) in dimethyl sulfoxide. However, the polymerization in the solvents such as N, N'-dimethyl-2-pyrrolidone, hexamethylphosphoramide, and N,N'-dimethylformamide, and the polymerization with the other bisphenols $HO–C_6H_4–X–C_6H_4–OH$, where $X = CO$, SO_2, $CH_3P(O)$, $C_6H_5P(O)$ in place of BPA gave gumlike polymers. The polymer prepared from BCPO and BPA did not decompose up to ca. 300°C under air or nitrogen atmosphere, but it decomposed slowly at 300-520°C, and decomposed rapidly at 520-540°C. The activation energy (ΔE) for the maximum rate of weight loss was 47.8 kcal/mole.

INTRODUCTION

It is well known that poly(arylene ethers) such as polysulfone exhibit excellent mechanical properties and stabilities to heat and numerous chemicals [1-21].

Johnson et al. have reported in detail the chemistry of polymer preparation and thermal properties [1-3]. Hale et al. [2] and others [4, 5] have indicated that a mixed aromatic sulfone-ether polymer is more stable than an aromatic sulfone and carbonate polymers, but not as stable as a simple aromatic polyether. As these results are very interesting to us, we attempted to prepare polymers having a phenylphosphinylidene group in the main chain by high-temperature solution polycondensation of bis(p-chlorophenyl)phenylphosphine oxide with the sodium salt of several bisphenols. In this paper, we wish to report the conditions of polymerization and properties such as thermal stability.

EXPERIMENTAL

Materials

Bis(p-chlorophenyl)phenylphosphine oxide (BCPO). BCPO was prepared from phenylphosphonic dichloride and p-chlorophenylmagnesium chloride according to the method described by Kumada et al. [22]. In the infrared spectrum, the characteristic absorption bands due to C_6H_5 at 1600 and 1500 cm^{-1}, p-substituted C_6H_4 at 820 cm^{-1}, C–Cl at 760 and 1090 cm^{-1}, P=O at 1200 cm^{-1}, and P–C_6H_4 at 1120 and 1140 cm^{-1} were observed; in the mass spectrum the following fragment peaks were observed: m/e 346 (M^+), 348 ($M^+ + 2$), 350 ($M^+ + 4$), 311 (M - Cl), and 235 (M - C_6H_4Cl). The product melted at 107-108°C (lit. [22] mp 104.5-105.0°C).

Bisphenols. Bisphenol A (BPA) and bisphenol S were purified by recrystallization from toluene. Their melting points were 157-158°C and 250-251°C, respectively. The preparation of bis(p-hydroxyphenyl)phenylphosphine oxide, and bis(p-hydroxyphenyl)methylphosphine oxide, and p,p'-dihydroxybenzophenone were carried out by the procedure previously reported [23]. Their melting points were 96-97°C, 261-262°C, and 212-213°C, respectively.

Solvents. Dimethyl sulfoxide (DMSO), N,N'-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA), and nitrobenzene were purified by vacuum distillation, and stored over 3 Å molecular sieves. Their boiling points were 77-78°C/15 Torr, 76°C/39 Torr, 96-98°C/6 Torr, and 86°C/10 Torr, respectively.

Polymerization Procedure

The synthesis of phosphorus-containing polyethers was carried out by solution polycondensation under a nitrogen atmosphere. A typical procedure was as follows.

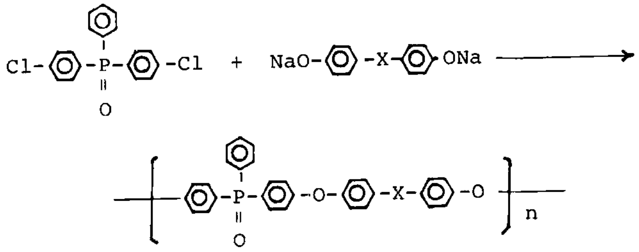
In a flask were placed 0.228 g (1 mmole) of bisphenol A, 2.00 ml (2 mmole) of 1 N aqueous sodium hydroxide, and 2 ml of benzene. The mixture was heated at about 75°C for 2 hr until BPA was dissolved completely with stirring, and maintained at 130-140°C to remove water from the mixture by distillation as the benzene-water azeotrope. The small amount of water left in the mixture was then removed under reduced pressure (25 Torr). To the resulting salt of BPA, 0.347 g (1 mmole) of BCPO in 3 ml of DMSO was added dropwise with vigorous stirring, and the reaction mixture was maintained at 170°C for 10 hr. The polymer was precipitated by pouring the mixture into a large volume of water, collected by filtration, washed well with methanol and water, and dried at 100°C in a vacuum oven until the weight became constant.

Analysis. Calcd. for $C_{33}H_{27}O_3P$: C, 78.87%; H, 5.42%; P, 6.16%. Found: C, 78.57%; H, 6.02%; P, 6.01%.

RESULTS AND DISCUSSION

Preparation of Phosphorus-Containing Polyethers

The polymers were prepared from BCPO and bisphenols in the presence of alkali by a high-temperature solution method.



X: $(CH_3)_2C$, CO, SO_2, $CH_3P(O)$, $C_6H_5P(O)$

The amounts of alkali on the polycondenstaion of BCPO with BPA were examined, and the results are shown in Table 1. As expected, the polyether having the highest viscosity, $\eta_{sp}/c = 0.15$, was obtained when stoichiometric amounts were used, but the viscosities of polymers

TABLE 1. Effect of Amount of NaOH[a]

Run	[NaOH]/[BPA][b]	Yield (%)	PMT (°C)	η_{sp}/c[c]
1	1.754	90	166-173	0.09
2	1.858	91	175-181	0.12
3	1.944	87	194-200	0.13
4	2.000	84	208-213	0.15
5[d]	2.000	48	180-185	0.11
6	2.038	84	205-210	0.14
7	2.122	85	184-188	0.12
8	2.358	89	151-157	0.06

[a] In each run, 1 mmole of BCPO, 1 mmole of BPA, and 3 ml of DMSO were used; reaction temperature, 175°C; reaction time, 10 hr.

[b] Molar ratio of NaOH to BPA.

[c] c = 0.5 g/100 ml, in m-cresol at 30°C.

[d] KOH was used.

TABLE 2. Effect of Reaction Temperature[a]

Run	Temperature (°C)	Yield (%)	PMT (°C)	η_{sp}/c
1	155	83	178-184	0.11
2	165	81	188-193	0.12
3	175	84	208-213	0.15

[a] In each run, 1 mmole of BCPO, 1 mmole of BPA, 2 mmole of NaOH, and 3 ml of DMSO were used; reaction time, 10 hr.

[b] c = 0.5 g/100 ml, in m-cresol at 30°C.

decreased by using stoichiometrically more or less amounts of alkali to BPA. Since this type reaction proceeds via nucleophilic attack on the aromatic carbon by phenate [1, 24], the excess hydroxide ion should lead to hydrolysis of BCPO. Therefore, the stoichiometric amount of NaOH to bisphenols was employed for all subsequent polymerizations. The use of KOH in place of NaOH gave lower viscosity and yield.

TABLE 3. Effect of Solvents[a]

Run	Solvent	Dielectric constant ε^b	Reaction temp (°C)	Yield (%)	PMT (°C)	η_{sp}/c^c	Appearance
1	Nitrobenzene	34.9	190	-	-	-	Deep brown, viscous oil
2	Nitrobenzene	34.9	140	59	-	-	Slightly brown gum
3	DMF	36.7	140	86	58-59	-	Slightly brown powder
4	NMP	32.0	180	90	155-164	0.07	Slightly brown powder
5	HMPA	30.0[d]	194	35	74-83	-	Deep brown powder
6	DMSO	46.7	175	84	208-213	0.15	White powder

[a] In each run, 1 mmole of BCPO, 1 mmole of BPA, 2 mmole of NaOH, and 3 ml of solvent were used; reaction time, 10 hr; reaction temperature, 175°C.

[b] At 25°C unless otherwise noted.

[c] $c = 0.5$ g/100 ml, in m-cresol at 30°C.

[d] At 20°C.

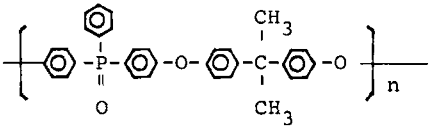
Second, temperature effect was examined. As shown in Table 2, the viscosities of polymers increased as the reaction temperature was raised. The results are attributable to the increase of polymerization rate with increasing temperature.

In Table 3, the effect of solvents on polymerization are shown. When DMSO was used, the polymer having the highest viscosity and polymer melting point (PMT) was obtained. These results are reasonably explained from the facts that DMSO is an excellent solvent for a variety of inorganic as well as organic compounds [25] and increases the rates of bimolecular nucleophilic reactions of the type presented here [25, 26]. When solvents other than DMSO were used, colored polymers of lower viscosity and PMT were obtained. Presumably, these results might be ascribable to the fact that reaction between reactants and solvent occurs.

The polymerizations with various bisphenols other than BPA were also examined. These polymerizations proceeded with difficulty to form the expected polymers and resulted in gummy polymers. It is concluded that the results depend on the lower nucleophilicity of phenates having an electron-withdrawing groups connecting the benzene rings. The tendency was similar to that observed in the preparation of polyethers from 4,4'-dichlorodiphenyl sulfone [1].

Structure of Phosphorus-Containing Polyethers

The polymer obtained from BCPO and BPA was identified by its infrared and NMR spectra and from results of elemental analysis. It showed characteristic absorption bands due to –O– at 1240 cm^{-1}, $P–C_6H_4$ at 1120 cm^{-1} and 1140 cm^{-1}, $–C(CH_3)_2–$ at 1170 cm^{-1}, C_6H_5 at 1500 and 1600 cm^{-1}, p-substituted C_6H_4 at 830 cm^{-1}, and P=O at 1275 cm^{-1}. The NMR spectrum of the polymer showed a singlet for the $–C(CH_3)_2–$ protons at δ = 1.64 ppm and a complex splitting pattern for the $C_6H_5–P$ and $C_6H_4–P$ protons at δ = 6.50-7.92 ppm. It is clearly apparent that the polymer is composed of the structural unit I.



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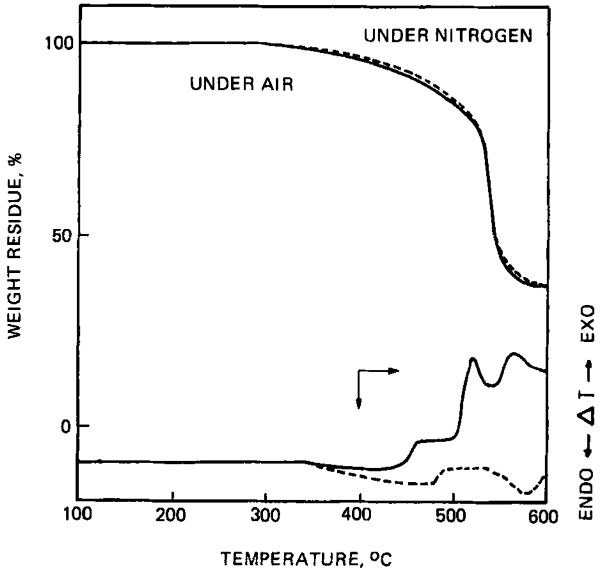

FIG. 1. Results of DTA and TGA of polyether.

Properties of Polyether

The thermal properties of phosphorus-containing polyether ($\eta_{sp}/c = 0.15$) obtained from BCPO and BPA was examined by means of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) under air or nitrogen. The results of these examinations are shown in Fig. 1. The polymer begins to show a weight loss at around 300°C, and shows marked decomposition in the range of 520-540°C, which correlates well with an exothermic peak at 520°C in air. The fact that the shape of the TGA curve under air is similar to that under nitrogen shows that the degradation of the polymer is apparently not affected by oxygen.

The apparent activation energy (ΔE) for thermal degradation was 47.8 kcal/mole, as obtained from the decline in weight at various rates of temperature rise measured in a nitrogen gas flow by the method of Ozawa [27].

TABLE 4. Solubility of the Phosphorus-Containing Polyether[a]

Solvent	Solubility[b] At room temperature	 On heating
Methyl ethyl ketone	±	+
Methanol	±	±
n-Dibutyl ether	-	-
Acetonitrile	-	±
Dioxane	±	+
Formic acid	-	±
Benzene	±	+
Nitrobenzene	+	++
DMSO	+	++
HMPA	+	++
Chloroform	+	++
Trichloroethylene	+	++
Dichloroethylene	+	++
Ethylene chloride	+	++

[a] Obtained from BCPO and BPA.

[b] Solubility: (++) highly soluble; (+) soluble; (±) partially soluble or swelling; (-) insoluble.

The solubility of polymer is shown in Table 4. The polymer was soluble in polar aprotic solvents and halogenated hydrocarbons and was partially soluble in solvents such as methanol, benzene, and n-dibutyl ether.

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