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(Received December 26, 1988)

ADDITIVE EFFECT OF PHOSPHORUS COMPOUNDS UPON THE PREPARATION OF COPOLY(ESTER-AMIDE)S BY DIRECT POLYCONDENSATION USING DIPHENYL CHLOROPHOSPHATE

By Fukuji Higashi and Hideo Arikawa

(Department of Polymer Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184 Japan)

ABSTRACT

The direct polycondensations of aromatic dicarboxylic acids, bisphenols, and diamines using diphenyl chlorophosphate in the presence of phosphorus compounds were studied. Addition of the phosphorus compounds prevented effectively the gelation of the reaction mixture and produced soluble copolymers even if a high molar percentage of diamines was added. Based on the NMR study, it is considered that the reactivity of the phenolic groups of bisphenols increased due to the hydrogen-bond association with the phosphorus compounds resulting in change of the relative reactivity to diamines. This may lead to favorable monomer sequences in copolymers for the improvement of solubility and the prevention of gelation in the reaction mixture. The changes of monomer sequences caused by the phosphorus compounds were investigated also in terms of optical anisotropy of the copolymers prepared from isophthalic and terephthalic acids, methylhydroquinone, and diamines.

1. INTRODUCTION

We have shown a successful preparation of high molecular weight copoly(ester-amide)s by the direct polycondensation of aromatic dicarboxylic acids, bisphenols, and diamines using diphenyl chlorophosphate (DPCP) in pyridine.^{1,2)} The reaction proceeded homogeneously without gelation by sequential addition of bisphenols and then diamines, giving soluble copolymers of various combinations of bisphenols and relatively high molar % diamines. These facts were assumed to be due to favorable sequences of monomers in the copolymers, which were roughly estimated from optically anisotropic characteristics of the copolymers prepared from isophthalic (IPA) and terephthalic (TPA) acids, methylhydroquinone (MeHQ), and diamines.³⁾

Without the troublesome procedure of stepwise addition of the monomers as mentioned above, simultaneous addition also might change the sequences, when the relative reactivity of bisphenols to diamines could be modified by complexation with some reagents. Gramstad⁴⁾ showed strong hydrogen-bond association of phenols especially with phosphorus compounds. Among phos-

phorus compounds, phosphine oxides had high associating ability.

To examine the effect of complexation of monomers with phosphorus compounds upon the monomer sequences of the resulting copolymers and therefore upon their solubility, we carried out the copolycondensation of IPA, TPA, bisphenols, and diamines using DPCP and triphenylphosphine oxide (TPPO) which is commercially available and easy to handle. The sequences of the copolymers obtained were studied in terms of their solubility and optical anisotropic characteristics.

2. RESULTS AND DISCUSSION

Copolycondensations of IPA, 50 mol % TPA, bisphenols, and diamines in pyridine were carried out by the slow addition of a pyridine solution of a mixture of bisphenols, diamines, and TPPO, as described in the previous paper.³⁾ Optical anisotropies of the copolymers obtained were determined by the temperature above which complete birefringence was observed under zero shear by use of a polarizing microscope equipped with a hot-stage.

Copolycondensation of IPA, TPA, 2, 2-bis (4-hydroxyphenyl)propane (BPA), and 50 mol % of 4,4'-oxydianiline (ODA) was carried out in the presence of TPPO (Table 1). As previously reported,²⁾ simultaneous addition of BPA and ODA resulted in the gelation to give an insoluble copolymer whereas the sequential addition of BPA and then ODA gave a soluble copolymer without gelation. However, when TPPO was present, the reaction, even upon the spontaneous addition of BPA and ODA, proceeded homogeneously and gave a soluble copolymer with high inherent viscosity.

Table 1 Additive Effect of TPPO on the copolycondensation of IPA, TPA, BPA, and 50 mol % ODA in Pyridine^{a)}

TPPO(mmol)	State	$\eta_{\text{inh}}^{\text{c)}$
0	Gelation	Insoluble
0 ^{b)}	Solution	1.40
5	Solution	1.33
10	Solution	1.14

a) TPA, IPA, BPA, ODA = 2.5 mmol; DPCP = 12mmol; Py = 30 ml; addition of BPA/ODA/TPPO = 20 min.

b) The reaction was carried out by sequential addition of BPA for 5 min and then ODA for 5 min.

c) Measured in 60:40 phenol/*sym*-tetrachloroethane (PTCE) at 30°C.

The copolycondensations with 50-90 mol % ODA were carried out in the presence of an equivalent amount of TPPO with respect to hydroxy groups of BPA (Table 2). In the copolycondensations with more than 60 mol % ODA in the absence of TPPO, gelation occurred by both simultaneous and sequential addition of BPA, and ODA, and the resulting copolymer with 80 mol % ODA, for example, was insoluble in 60: 40 phenol/ *sym*-tetrachloroethane(PTCE) : only the copolymer prepared by sequential addition was soluble in *p*-chlorophenol. However, the reaction using more than 80 mol % ODA in the presence of TPPO gave copolymer which was soluble in PTCE or in DMAc/ LiCl (5 %) solvent.

As described above, the gelation of the reaction mixture and the solubility of the copolymers prepared by the simultaneous addition of BPA and ODA were significantly improved by the presence of TPPO as well as by the sequential addition of BPA and ODA. These facts led us to consider that TPPO might promote the reactivity of BPA via hydrogen-bond association even in the presence of ODA so that alcoholysis with BPA might occur easily, as observed by the initial reaction of BPA in the sequential addition.

The association of the phosphorus compounds with phenol was studied by means of IR spectroscopy. The association constant, K_{ass} for the association of phenol with TPPO and with triethylphosphine oxide determined at 20°C in carbon tetrachloride were 1055.4 and 2522.0, respectively, showing that the latter has higher ability of the association than the former. Tributylphosphine oxide may have high K_{ass} and association ability as those of triethylphosphine oxide, though it has not been reported.

Table 2 Additive Effect of TPPO on the Copolycondensation of IPA, TPA, BPA, and Several mol % ODA in Pyridine^{a)}

ODA (mol %)	This work		Previous work ³⁾			
	simultaneous addition		simultaneous addition		sequential addition	
	State	$\eta_{\text{inh}}^{\text{b)}$	State	$\eta_{\text{inh}}^{\text{b)}$	State	$\eta_{\text{inh}}^{\text{b)}$
50	Solution	1.15	Solution	1.38	Solution	1.40
80	Solution	1.28	Gelation	Insoluble	gelation	1.26 ^{d)}
90	Solution	1.75 ^{c)}	—	—	—	—

a) IPA, TPA = 2.5 mmol; BPA + ODA = 5mmol; DPCP = 12 mmol; TPPO = 10 mmol; Py = 30 ml; simultaneous addition of BPA/ODA/ TPPO = 10 min; simultaneous addition of BPA/ ODA for 10 min, and sequential addition of BPA for 5 min and then ODA for 5 min in previous work.³⁾

b) Measured in 60:40 phenol/*sym*-tetrachloroethane at 30°C.

c) Measured in DMAc/LiCl (5%) at 30°C.

d) Measured in *p*-chlorophenol at 50°C.

In this experiment we examined the association of several phosphorus compounds with BPA and ODA in pyridine by means of NMR spectroscopy. Similar phenomena were also observed in NMR spectra as shown in Table 3. BPA in pyridine showed a peak at 11.23 ppm

Table 3 Proton Shifts of Phosphorus Compound-BPA Complexes in Pyridine^{a)}

Phosphorus compound	δ -value (ppm)
None	11.23
Triphenyl phosphate	11.29
Trimethyl phosphate	10.99
Triphenylphosphine oxide	10.99
Tributylphosphine oxide	10.66
Hexamethylphosphoramide	10.66

a) Measured in pyridine solution that contained 10 wt% BPA (5 mmol), phosphorus compounds (10 mmol), and TMS as internal reference at room temperature.

due to phenolic protons. When the phosphorus compounds with higher ability to form intermolecular hydrogen bonds with phenol were present, the peak shifted to much higher magnetic fields. On the other hand, no substantial change in the NH_2 peak at 5.14 ppm was observed by addition of the phosphorus compounds.

To investigate complexation effect of TPPO on the monomer sequences in copolymers in terms of the charac-

Table 4 Copolycondensation of IPA, TPA, MeHQ, and 20 mol % ODA in the Presence of TPPO in Pyridine^{a)}

TPPO (mmol)	Birefringence (°C)	State	η_{inh}^b
None	>260	Precipitation	1.07
5	>250	Less precipitation	1.23
10	>240	Less precipitation	1.17

a) IPA, TPA = 2.5 mmol; MeHQ = 4 mmol; ODA = 1 mmol; DPCP = 12 mmol; Py = 30ml; time for addition of MeHQ/ODA/TPPO = 10 min.

b) Measured in *p*-chlorophenol at 50°C.

teristics other than gelation and copolymer solubility, the copolycondensation of IPA, TPA, MeHQ, and 20 mol % ODA was carried out in the presence of TPPO. The copolymer was found to show optical anisotropy at a temperature above 260 °C, when prepared by the reaction with DPCP.³⁾ The reaction in the presence of TPPO was accompanied by less precipitation than the case of

Table 5 Copolycondensation of IPA, TPA, MeHQ, and 20 mol % ODA in the Presence of Several Phosphorus Compounds^{a)}

Phosphorus compound	Birefringence (°C)	η_{inh}^b
None	>260	1.07
Triphenylphosphine oxide	>240	1.17
Tri- <i>n</i> -butylphosphine oxide	>220	0.98
Hexamethylphosphoramide	>225	0.63

a) IPA, TPA = 2.5mmol; MeHQ = 4 mmol; ODA = 1mmol; DPCP = 12 mmol; phosphorus compound = 10 mmol; Py = 30 ml; time for addition of MeHQ/ODA/phosphorus compound = 10 min.

b) Measured in *p*-chlorophenol at 50°C.

without TPPO, and gave a copolymer exhibiting optical anisotropy at lower temperatures, suggesting the formation of the copolymer with different solubility and thermal properties (Table 4). Similarly, the copolycondensations were carried out in the presence of one equivalent of several phosphorus compounds with respect to monomers (Table 5). The resulting mixtures were viscous solutions with some precipitates so that they were all diluted with about three times of pyridine to give copolymers in quantitative yield. Although one of the copolymers prepared in hexamethylphosphoramide (HMPA) showed a somewhat low inherent viscosity, other copolymers may have high enough molecular weight to discuss their optically anisotropic characteristics regardless of the effect of the molecular weight on the anisotropy. The resulting copolymers exhibited anisotropic melts at temperatures lower than 260 °C which was corresponding to the anisotropic melting temperature for the copolymer prepared in the absence of the phosphorus compounds.

Judging from the NMR data for the hydrogen-bonding association of BPA with phosphorus compounds listed in Table 3, the phosphorus compounds with higher ability of association gave the copolymer showing the anisotropy at lower temperatures. This may be due to significant promotion of the reactivity of MeHQ, leading to the random sequences of ODA in the copolymer even by simultaneous addition of MeHQ and ODA.

Copolycondensations of IPA, TPA, MeHQ, and 20 mol % ODA were conducted in the presence of TPPO to examine the effect of the basicity (nucleophilicity) of diamines on the optical anisotropy of

Table 6 Copolycondensations of IPA, TPA, MeHQ, and 20 mol % Various Diamines in the Presence of TPPO^{a)}

Diamine ^{b)}	Birefringence ^{c)} (°C)	$\eta_{inh}^{c,e)}$
ODA	>240(>230)	1.17(1.12)
MDA	>260(>240 ^{d)})	0.92(1.0)
TDA	>270(>260)	0.86(0.89)
PPD	>300(>300)	0.89(1.24)

a) IPA, TPA = 2.5 mmol; MeHQ = 4 mmol; diamine = 1 mmol; DPCP = 12 mmol; TPPO = 10 mmol; Py = 30 ml; time for addition of MeHQ/diamine/TPPO = 10 min.

b) ODA = 4,4'-oxydianiline; MDA = 4,4'-methylenedianiline; TDA = 4,4'-thioxydianiline; PPD = *p*-phenylenediamine.

c) Values in parentheses were obtained by the reaction of sequential addition of MeHQ and diamines in the absence of TPPO.³⁾

d) Partially birefringent without shear, but completely under shear.

e) Measured in *p*-chlorophenol at 50°C.

the resulting copolymers, and results were compared with those previously obtained by sequential addition of MeHQ and diamines in the absence of TPPO (Table 6). The results of this experiment were nearly comparable to those in the previous work, suggesting that the reaction of MeHQ was facilitated by TPPO as favorable as achieved by sequential initial addition of MeHQ. It is interesting to note that the copolymer with 4,4'-methylenedianiline (MDA) showed complete anisotropy above 260°C, despite the fact that only partial anisotropy was observed for the copolymer prepared by sequential addition. These facts indicate that TPPO and other phosphorus compounds promote the formation of re-

latively highly homogeneous copolymers instead of being contaminated by some amounts of block copolymer.

3. EXPERIMENTAL

Copolycondensations of IPA, TPA, Bisphenols, and Diamines in the Presence of Phosphorus Compounds

A mixture of DPCP (12 mmol), IPA (2.5 mmol), and TPA (2.5 mmol) in pyridine (20 ml) prepared as previously described²⁾, was maintained at room temperature for 20 min and then at 120 °C (bath temperature) for 10 min. To the hot solution, a pyridine solution of bisphenols (0.5-4 mmol), diamines (4.5-1 mmol), and phosphorus compounds (0-10 mmol) was added dropwise over 10-20 min, and the whole mixture was further heated at 120°C for 3 h. The resulting mixtures were diluted with pyridine and poured into methanol to isolate the copolymers, and the precipitated polymers were filtered and washed with boiling methanol. The dried and pulverized samples were subjected to anisotropic measurement. The anisotropy was determined by the temperature above which complete birefringence was observed under zero shear by use of a polarizing microscope equipped with a heating stage.

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クロルりん酸ジフェニルエステルを用いた直接重縮合による コポリエステルアミド合成におけるりん化合物の添加効果

東京農工大学工学部 東 福次, 蟻 川 英 男

りん化合物の存在下にクロルりん酸ジフェニルエステルを用いた芳香族ジカルボン酸、ビスフェノール、ジアミンの直接重縮合を検討した。りん化合物の添加でゲル化が防止でき、ジアミン含量の高い可溶性コポリマーも合成できた。NMRより、フェノール性水酸基の反応性がりん化合物との水素結合によって向上し、ジアミンとの

相対反応性が変化し、これらの結果、モノマー配列が変化して溶解性向上やゲル化防止に効果があると結論した。このモノマー配列の変化をイソフタル酸、テレフタル酸、メチルヒドロキノン、およびジアミンからのコポリマーの光学異方性からも検討した。