

# Novel UV Absorbers Prepared from 2,4-Dihydroxybenzophenone and Hexachlorocyclotriphosphazene

KENZO INOUE,\* HIROAKI TAKAHATA, and TEIICHI TANIGAKI

Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

## SYNOPSIS

The UV-stabilizing ability and thermal loss from the polystyrene film of novel UV absorbers, 2-[(3-hydroxy-4-benzoyl)phenoxy]pentachlorocyclotriphosphazene (HBPC) and hexakis[(2-hydroxy-4-benzoyl)phenoxy]cyclotriphosphazene (HBPP), were investigated. The UV-stabilizing ability of HBPC estimated by the formation of carbonyl groups in polystyrene was comparable to that of 2,4-dihydroxybenzophenone (DHB), suggesting that the phosphazene moiety does not affect the efficiency of the stabilizing ability of DHB units. No significant difference of efficiency per stabilizing units between HBPC and HBPP was observed. HBPC and HBPP are noteworthy for their low thermal losses from the polystyrene film, i.e., the thermal loss of HBPP was completely suppressed and the diffusion coefficient of HBPC at 160°C was two orders of magnitude smaller than that of DHB. The thermogravimetric analysis and differential scanning calorimetry measurement showed that HBPC and HBPP are nonvolatile and stable up to 230 and 300°C, respectively. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In the last few decades, intensive efforts have been made to understand the mechanism of photodegradation of polymers and to develop new stabilizers.<sup>1-5</sup> It is well recognized that the effectiveness of stabilizers in polymers is affected by several factors such as chemical activity, physical persistency, and compatibility. The incorporation of a UV-stabilizer moiety into a polymeric substrate is one of effective methods to minimize the loss of absorbers caused by the migration of these additives to a polymer surface and subsequent evaporation. However, these polymeric absorbers increase difficulties due to their limited compatibility with host polymers.

Hexachlorocyclotriphosphazene (HCP) has attractive features since the properties of phosphazenes can be varied in a large range, depending on the structures of introducing organic groups and their number.<sup>6-8</sup> If a phosphazene derivative with

one stabilizing moiety can be prepared and acts efficiently, it should easily be modified so as to be compatible with a particular host polymer by the replacement of remaining chlorine atoms with suitable organic groups. This replacement should accompany a favorable increase in the molecular weights of stabilizers. Furthermore, the cyclophosphazenes that have thermally stable properties might contribute to improve thermal properties of a stabilizer. In this paper, we report a part of our program to synthesize a new class of stabilizers by utilizing hexachlorocyclotriphosphazene, a preparation of 2-[(3-hydroxy-4-benzoyl)phenoxy]pentachlorocyclotriphosphazene (HBPC) and hexakis[(2-hydroxy-4-benzoyl)phenoxy]cyclotriphosphazene (HBPP), and their stabilizing ability and thermal loss from the polystyrene film.

## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene (HCP, Nihon Soda Co.) was recrystallized from *n*-hexane. 2,4-Dihy-

\* To whom correspondence should be addressed.  
Journal of Applied Polymer Science, Vol. 50, 1857-1862 (1993)  
© 1993 John Wiley & Sons, Inc. CCC 0021-8995/93/111857-06

droxybenzophenone (DHB) was used as received. Polystyrene was prepared by radical polymerization with an AIBN initiator.

### 2-[(3-Hydroxy-4-benzoyl)phenoxy]-pentachlorocyclotriphosphazene (HBPC)

A solution of DHB (10 g, 0.047 mol) and triethylamine (8.5 g, 0.084 mol) in 100 mL of benzene was added dropwise into a stirred solution of HCP (19.6 g, 0.056 mol) in 100 mL of benzene at room temperature. After stirring for 7 h, the resulting amine hydrochloride was filtered off and the solvent was removed under reduced pressure. HBPC was separated with a silica gel column (10 : 1 = hexane/benzene) and recrystallized from hexane. Yield: 9.3 g (38%). Mp 99–100°C. IR (nujol): 3430, 1625, 1600, 1240  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS): 12.2 (s, 1 H, —OH), 7.7–6.6 (m, 8 H, arom. H) ppm.

ANAL: Calcd. for  $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_3\text{P}_3\text{Cl}_5$ : C, 29.70%; H, 1.73%; N, 8.00%.

Found: C, 29.51%; H, 1.45%; N, 7.73%.

### Hexakis[(3-hydroxy-4-benzoyl)phenoxy]-cyclotriphosphazene (HBPP)

HBPP was prepared by a method similar to that described above, from DHB (20 g, 0.093 mol) and HCP (4.6 g, 0.013 mol) in the presence of triethylamine (20 g, 0.2 mol) in benzene. The reaction mixture was refluxed for 140 h. After the usual workup, the residue was dissolved in  $\text{CHCl}_3$ , and the solution was poured into hexane to precipitate HBPP. HBPP was recrystallized from methanol–acetone (1 : 1). Yield: 9.5 g (51%). Mp 142–144°C. IR (nujol): 3450, 1620, 1585, 1565, 1240, 1210, and 1160  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS): 12.2 (s, 6H, —OH), 7.7–6.4 (m, 48 H, arom. H) ppm.

ANAL: Calcd. for  $\text{C}_{78}\text{H}_{54}\text{N}_3\text{O}_{18}\text{P}_3$ : C, 66.24%; H, 3.85%; N, 2.97%.

Found: C, 66.14%; H, 3.74%; N, 3.14%.

### Stabilizing Ability

Weighed amounts of polystyrene and the absorber were dissolved in THF and cast into clear films (thickness,  $27 \pm 1.5 \mu\text{m}$ ). The films were irradiated in a merry-go-round-type apparatus with light ( $> 310 \text{ nm}$ ) from a 400 W high-pressure Hg lamp at a given time. The photooxidation was followed using IR spectra.

### Determination of Diffusion Coefficient

A typical experiment was as follows: Polystyrene film containing HBPC (1 mol %) was placed in a

oven maintained at 160°C. After a definite time, the film was dissolved in dichloromethane. The amount of the desorbed absorber was calculated from the difference of UV absorption at 327 nm before and after heating. The diffusion coefficient was calculated from eqs. (1) and (2) (*vide infra*).<sup>9</sup>

### Measurements

Infrared spectra were recorded with a Shimadzu IR 420 spectrophotometer.  $^1\text{H-NMR}$  spectra were obtained from a JEOL PMX60si instrument. UV spectra were recorded with a Shimadzu UV 260 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Nihon Bunko 880-PU, equipped with Shimadzu HSG 60/30 columns, using THF as the eluent. The columns were calibrated with monodisperse polystyrene standards. Differential scanning calorimetry (DSC) measurement and thermogravimetric analysis were carried out using a Shimadzu DSC-50 and a Shimadzu T-30 system. Measurements were made in an atmosphere of nitrogen at a heating rate of 10°C.

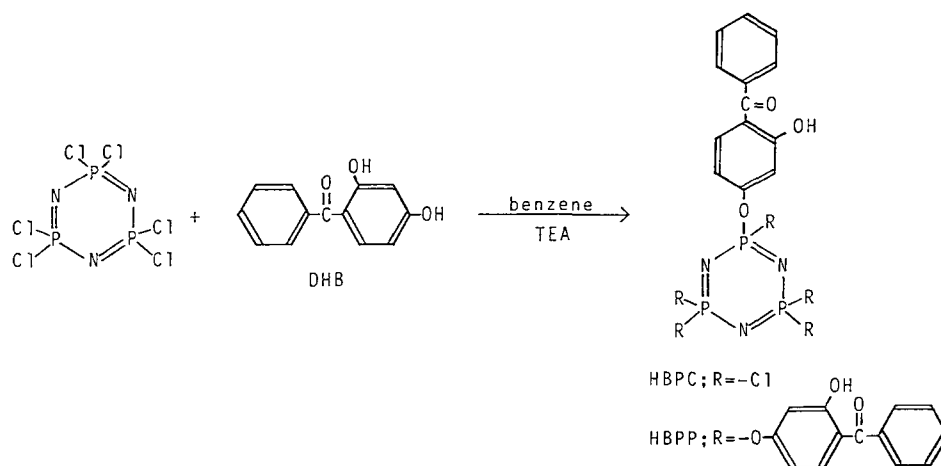
## RESULTS AND DISCUSSION

### Preparation and Properties of Absorbers

HBPC was easily prepared by the reaction of HCP with DHB in the presence of triethylamine at room temperature (Scheme 1). The total replacement of chlorine atoms with DHB could be achieved in a moderate yield when the reaction was carried out at 80°C for 6 days. The absorbers obtained are soluble in a number of organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , THF, and toluene.

HBPC and HBPP were characterized by a combination of IR, UV,  $^1\text{H-NMR}$ , and elemental microanalysis. The UV spectra of HBPC and HBPP showed a characteristic band in the 300–380 nm region (Fig. 1). The extinction coefficient at 327 nm for HBPC or at 329 nm for HBPP was significantly low and the absorption by  $\pi-\pi^*$  transition shifted to a short wavelength, compared to those of DHB. These behaviors have been reported for substituted hydroxybenzophenones at the 4-position.<sup>10,11</sup>

Cyclotriphosphazenes are well known to be thermally stable. As shown in Figure 2, the DSC profile of HBPC showed an endothermic peak corresponding to  $T_m$  at 99°C and an exothermic peak due to the decomposition at 230°C. An endothermic peak due to evaporation was not observed. A similar pattern was observed for HBPP. For the thermogravimetric analysis, HBPC and HBPP remained without any change of their weights up to 230 and



Scheme 1

300°C, respectively, while DHB began to vaporize at 170°C (Fig. 3). Thus, the substitution of the 4-position in DHB with the cyclophosphazene brings about favorable thermal properties, nonvolatility, and stability of resulting UV absorbers. Allcock et al.<sup>12</sup> demonstrated that the cyclophosphazenes have the capability to withstand the UV irradiation without suffering ring cleavage. In fact, for the photoirradiation of the polystyrene films containing HBPC or HBPP at 40°C for 20 h, decomposition products of stabilizers were not detected by TLC analysis.

### Stabilizing Ability

Polystyrene films containing HBPC and HBPP were clear and transparent. The formation of the carbonyl group during photoirradiation is one of parameters

to estimate the ability of absorbers. Figure 4 shows the change in the relative absorption of 1720–1870  $\text{cm}^{-1}$  as a function of irradiation time.

The formation of the carbonyl group was suppressed by the addition of HBPC (1 mol %) and the degree of which was comparable to that of DHB. When a 0.17 mol % of HBPP was used, almost the same stabilizing ability was obtained. Similarly, no significant difference of carbonyl formation between polystyrene with 6 mol % of HBPC and with 1 mol % of HBPP was observed. The ability of absorbers were also estimated by the change of molecular weight of polystyrene before and after irradiation (Table I).

The number-average molecular weight of polystyrene without an absorber changed from  $\bar{M}_n =$

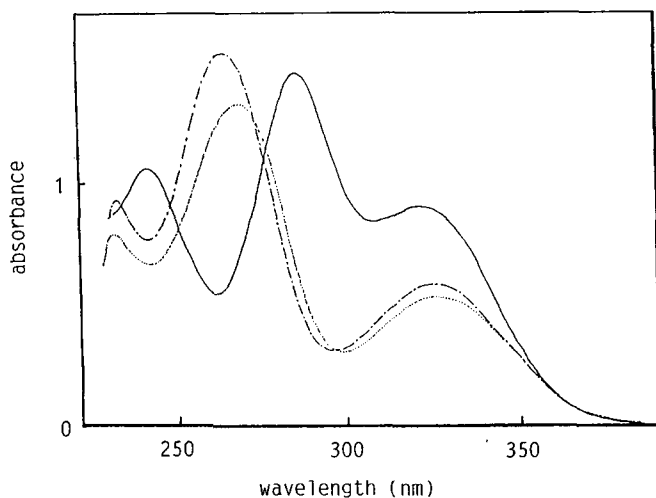


Figure 1 UV spectra of (—) DHB, (---) HBPC, and (.....) HBPP.

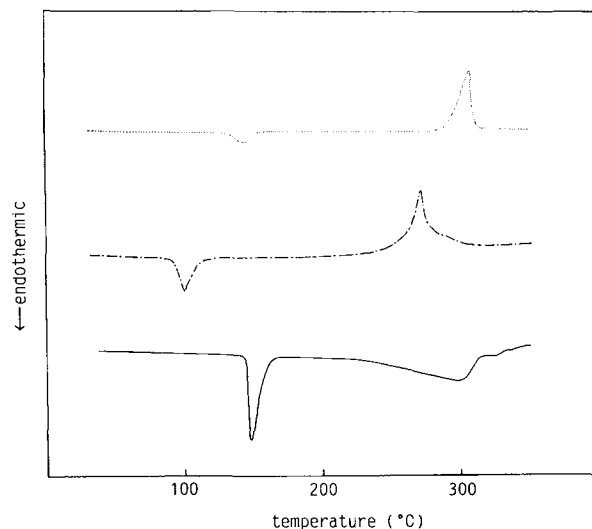
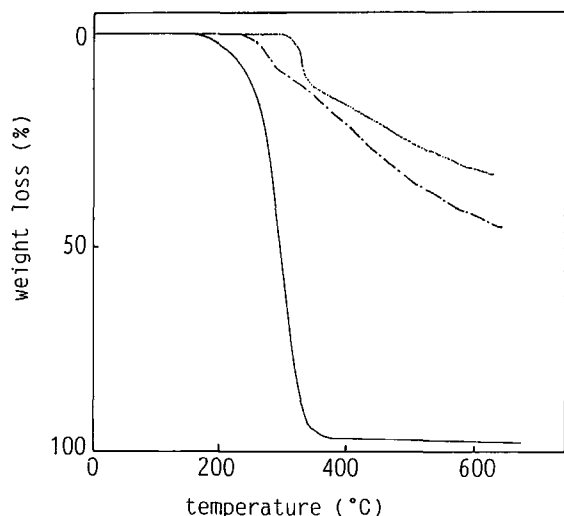
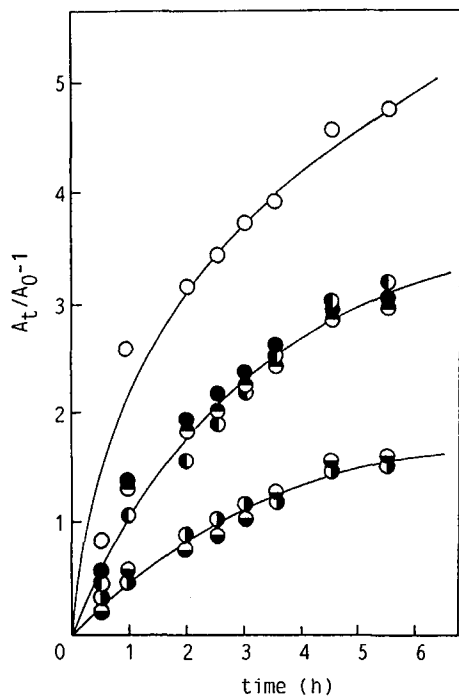


Figure 2 DSC profiles of (—) DHB, (---) HBPC, and (.....) HBPP.



**Figure 3** Thermogravimetric analysis of (—) DHB, (---) HBPC, and (· · · · ·) HBPP.

115,000 to  $\bar{M}_n = 63,000$ , together with the increase in polydispersity from  $\bar{M}_w/\bar{M}_n = 2.5$  to 4.1 under conditions. The addition of 1 mol % of HBPC and



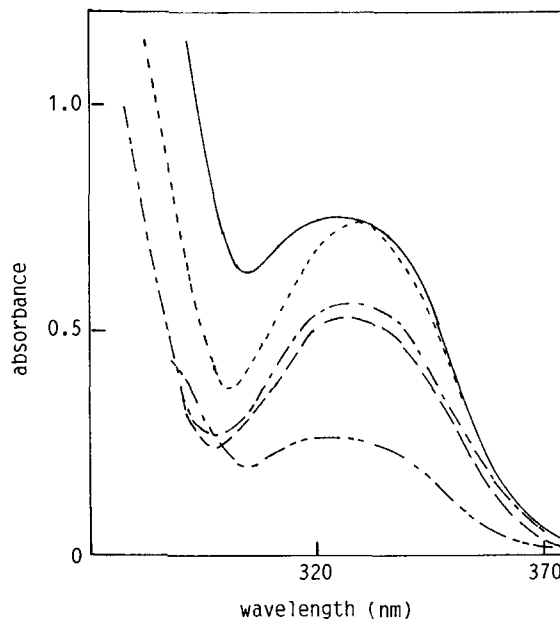
**Figure 4** Effects of absorbers on the formation of carbonyl groups as a function of irradiation time for unstabilized and stabilized polystyrenes. (O) Pure polystyrene; (●) DHB, 1 mol %, (●) 6 mol %; (●) HBPC, 1 mol %; (●) HBPP, 0.17 mol %; (●) 1 mol %.  $A_0$  and  $A_t$  indicate the relative intensity of IR spectra at  $1720\text{--}1870\text{ cm}^{-1}$ . Subscripts 0 and  $t$  denote before and after irradiation, respectively.

**Table I** Effects of UV Absorbers on the Molecular Weights of Polystyrene<sup>a</sup>

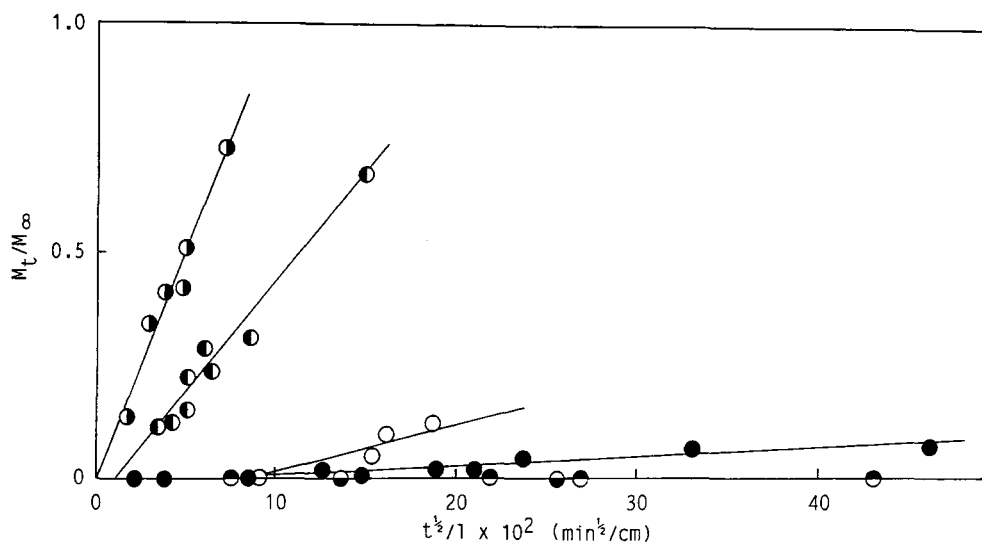
Absorber	Amount of Absorber		$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
	in Mol %			
—			6.3	4.1
DHB	1.00		9.1	2.9
	6.00		10.2	2.6
HBPC	1.00		8.4	3.0
HBPP	0.17		8.8	2.8
	1.00		10.0	2.7

<sup>a</sup> Molecular weight of polystyrene before irradiation,  $\bar{M}_n = 11.5 \times 10^4$ ,  $\bar{M}_w/\bar{M}_n = 2.5$ ; lamp, a 400 W high-pressure Hg lamp; time, 5.5 h.

0.17 mol % of HBPP apparently suppressed the decrease in the molecular weight and the increase in the polydispersity. These results indicate that the phosphazene moiety does not detract from the efficiency of DHB as a UV absorber. The results also suggest that tailor-made UV absorbers fitting with host polymers could easily be prepared by the replacement of remaining C1 atoms of HBPC with suitable organic groups, together with a favorable increase in molecular weights. The replacement of chlorine atoms in HBPC and functionality will be reported elsewhere.



**Figure 5** Change in UV spectra of polystyrene film with (—, · · · · ·) DHB, (---, ---) HBPC and (· · · · ·) HBPP. Irradiation time: (—) and (· · · · ·)  $t = 0$ , (---) and (---)  $t = 60$  min. The change of UV spectra of HBPP was not observed.



**Figure 6** Plots of  $M_t/M_\infty$  vs.  $t^{1/2}/l$  at temperature of (●, ●, ●) 140°C and (○, ○, ●) 160°C. (●, ●) DHB; (○, ●) HBPC; (●, ●) HBPP.

### Diffusion Coefficient

It is well known that the rate of diffusion of a UV absorber from a polymer film is strongly affected by molecular weight. HBPC and HBPP have relatively high molecular weights of 525 and 1414 g/mol, respectively, and, therefore, no or little thermal loss of these absorbers from a polymer film is expected. The polystyrene films containing DHB, HBPC, and HBPP were heated at 140°C for 60 min. As shown in Figure 5, HBPC was lost slowly compared to DHB, and no detectable loss of HBPP was observed.

Recently, Olson and Webb determined diffusion coefficients ( $D$ ) of UV absorbers from Bisphenol A (BPA)-polycarbonate using eqs. (1) and (2)<sup>9,13</sup>:

$$M_t/M_\infty = It^{1/2}/l \quad (1)$$

$$D = \pi/16I^2 \quad (2)$$

where  $t$  is the irradiation time;  $M_t$  and  $M_\infty$ , the amount of absorber desorbed during time  $t$  and a value of  $M_t$  for  $t = \infty$ ; and  $l$ , the film thickness.  $M_\infty$  could be assumed to be equal to the initial amount of absorber in the film. From the remaining amount of DHB and HBPC in the polystyrene film, which was measured by the spectroscopic method, the diffusion coefficient was determined. Plots of  $M_t/M_\infty$  vs.  $t^{1/2}/l$  gave straight lines for the DHB- and HBPC-polystyrene systems as shown in Figure 6.

When HBPC was used, an induction time was observed. HBPC is essentially liable to hydrolyze due to the involvement of reactive P—Cl group. In this experiment, the cast film on the glass was immersed to peel off in water. During the treatment,

it seems that the phosphazene ring suffers hydrolysis and the concentration of HBPC on or just beneath of the surface becomes low. This might be responsible for the induction time.

The  $D$  values of HBPC calculated from slopes were  $7.9 \times 10^{-11}$  cm<sup>2</sup>/min at 140°C and  $2.0 \times 10^{-9}$  cm<sup>2</sup>/min at 160°C. These values were found to be two and three orders of magnitude smaller than those of DHB ( $5.2 \times 10^{-8}$  cm<sup>2</sup>/min at 140°C and  $2.5 \times 10^{-7}$  cm<sup>2</sup>/min at 160°C). Even at 160°C, HBPP persists without any loss in the film. These results are most likely due to the increase in molecular weights by utilizing HCP.<sup>1,2,13</sup>

In summary, the UV absorbers prepared from DHB and HCP act as effective stabilizers and can persist in polystyrene. One of characteristic features of HBPC having almost the same efficiency as DHB is that the remaining P—Cl group could be utilized to design absorbers or stabilizers so as to possess properties such as thermal stability, high compatibility, and solubility with host polymers. Based on the concept, synthesis efforts are currently underway to prepare new stabilizers from cyclotriphosphazenes including HBPC.

### REFERENCES

1. J. Pospisil, *Angew. Makromol. Chem.*, **158/159**, 221 (1988).
2. J. Pospisil, *Adv. Polym. Sci.*, **101**, 65 (1991).
3. M. Minagawa, *Polym. Degrad. Stab.*, **25**, 121 (1989).
4. D. Bailey, D. Tirrell, C. Pinazzi, and O. Vogl, *Macromolecules*, **11**, 312 (1978).

5. G. Hauserman and M. Johnson, *J. Appl. Polym. Sci.*, **20**, 2533 (1976).
6. H. R. Allcock, *Chem. Eng. News*, **63**, 22 (1985).
7. K. Inoue, H. Nakamura, S. Ariyoshi, M. Takagi, and T. Tanigaki, *Macromolecules*, **22**, 4466 (1988).
8. C. W. Allen, J. C. Shaw, and D. E. Brown, *Macromolecules*, **21**, 2653 (1988).
9. T. Masuko, M. Sato, and M. Karasawa, *J. Appl. Polym. Sci.*, **22**, 1431 (1978).
10. B. Stutzel, T. Miyamota, and J. Cantow, *Polym. J.*, **8**, 247 (1976).
11. Z. Osawa, K. Matsui, and Y. Ogiwara, *J. Macromol. Sci. Chem. A*, **1**, 581 (1969).
12. J. P. O'Brien, W. T. Ferrar, and H. R. Allcock, *Macromolecules*, **12**, 108 (1979).
13. D. R. Olson and K. K. Webb, *Macromolecules*, **23**, 3762 (1990).

Received October 27, 1992

Accepted May 7, 1993