

Meta-Bromobiphenol Epoxy Resins: Applications in Electronic Packaging and Printed Circuit Board

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SYNOPSIS

Novel 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TBTMBP), and its epoxy derivatives, were synthesized to incorporate the stable meta-brominated phenol moiety into epoxy resin systems. In electronic encapsulation and laminate applications, epoxy systems derived from TBTMBP have exhibited superior hydrolytic and thermal stability as compared with the conventional ortho-brominated epoxy resins. These properties have resulted in an extended device life for semiconductors and a high T_g with excellent blister resistance for the printed circuit board, while meeting flame retardancy requirements as well.

INTRODUCTION

Epoxy resins containing bromine atoms are particularly useful in circuit boards, electrical laminate, potting, and encapsulation applications in which flame retardant properties are desired. Brominated resins that contain bromine atoms ortho- or para-, with respect to a glycidyl ether group or a hydroxyl group, have been proven to be the cause of inferior thermal stability and wire bond failure.¹⁻⁵

Brominated resins in which the bromine atom is in the meta position to the phenolic hydroxyl or the glycidyl ether group have been shown to be more hydrolytically and thermally stable than their ortho- or para-brominated counterpart.⁶⁻⁸ Unfortunately, very few meta-brominated bisphenols have been described in the literature. The aim of the present article is to describe the syntheses of novel meta-bromo-biphenol and its diglycidyl ether derivatives. Their superb performances in electronic packaging and printed circuit board applications are discussed.

EXPERIMENTAL

The glass transition temperatures (T_g) were determined by Differential Scanning Calorimetry using

a calibrated DuPont Instrument (Model No. 912 with a DuPont 1090 controller). Samples were heated under a nitrogen atmosphere at a rate of 10°C per min.

The dynamic decomposition properties were determined using a DuPont Thermal Gravimetric Analyzer (Model No. 951 with a DuPont 1090 controller). The dynamic mechanical properties were measured on a DuPont Dynamic Mechanical Analyzer (Model No. 982 with a DuPont 1090 controller).

The Blister Resistance Test

The $2\frac{1}{4}'' \times 3\frac{1}{4}''$ laminate samples were exposed to 15 psig steam in a pressure cooker for a specified amount of time. Samples were removed from the pressure cooker, were dried with a paper towel, and were immediately immersed in molten solder at 260°C for 20 s. Results were recorded by determining the number of nonblistered sides as divided by the total number of sides tested.

Preparation of 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TBTMBP)

To a 3-necked flask equipped with a stirrer, thermometer and reflux condenser, 24.2 g (0.1 mole) of 2,2',6,6'-tetramethyl-4,4'-biphenol, and 200 mL of methylene chloride were added. Upon stirring at

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room temperature to achieve a complete solution, 46 mL (0.9 mole) of bromine was added through a dropping funnel over a period of 10 min. The reaction temperature was allowed to increase to 40°C and was held at that temperature for 3 h. Excess bromine and solvent were removed by distillation, which resulted in a quantitative yield (55.7 g) of gray solid. Nuclear magnetic resonance (NMR) analysis of the solid did not detect any methyl bromination. Gas chromatographic analysis of the solid indicated 96% tetrabromotetramethyl biphenol and 4% tribromo compound. The crude product was further purified by slurring in 100 mL acetone and refluxing for 1 h. Filtration of the slurry at room temperature produced a white solid (51 g, 91.5% yield) of 98% purity with a melting point of 243–245°C. The proton nuclear magnetic resonance spectrum has the following signals: (DMSO d_6) δ ; 2.40 (s,12H), 7.51 (s,2H). Anal. Calcd. for $C_{16}H_{14}Br_4O_2$: C, 34.41; H, 2.51; Br, 57.34; O, 5.73. Found: C, 34.49; H, 2.54; Br, 57.16; O, 5.81.

Preparation of the Diglycidyl Ether of TBTMBP (DGE of TBTMBP)

To a 2-liter, 5-neck round bottom flask, equipped with a heating mantle, stirrer, thermometer, and reflux condenser, were added 300 g (0.54 moles) of 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol, 497.3 g (5.38 moles) of epichlorohydrin, 267.8 g of isopropyl alcohol, and 43.2 g of water. The mixture was heated to 65°C and 193.6 g (0.968 mole) of 20% aqueous sodium hydroxide was added dropwise over a period of 45 min while maintaining the reaction temperature at 65°C. After the completion of sodium hydroxide addition, the reaction mixture was maintained at 65°C for an additional 15 min. The organic phase was separated and further agitated with 86.4 g (0.43 moles) of 20% aqueous sodium hydroxide at 65°C for 30 min. The aqueous phase was separated from the organic phase and was discarded. The organic phase was washed several times with deionized water to remove the residual sodium chloride. The organic phase from water washes was placed on a rotary evaporator under a full vacuum at 150°C to remove the solvent completely. A pale yellow solid of the diglycidyl ether product (325.6 g) with an epoxy equivalent weight (EEW) of 374 was obtained.

Advancement of Epoxy Resin with TBTMBP

The diglycidyl ether of bisphenol-A (D.E.R. 331, the Dow Chemical Company) was reacted with

TBTMBP at 160°C for 90 min in the presence of 500 ppm of ethyltriphenylphosphonium acetate catalyst. The equivalent ratio of epoxy to phenol of 2.56 : 1 produced a solid epoxy resin with an EEW of 483.

Advancement of Epoxy Resin with Tetrabromobisphenol-A (TBBA)

The same advancement procedure described above was used. D.E.R. 331 was reacted with TBBA at an equivalent ratio, epoxy to phenol, of 2.54 : 1 to yield a solid epoxy resin with an EEW of 483.

High T_g of TBTMBP Epoxy Resin

Various epoxy resins were mixed with methylenedianiline at 150°C, poured into a hot aluminum mold, cured in an oven at 175°C for 1 h, and post-cured at 200°C for 2 h. The amounts of epoxy resins, curing agent, and the glass transition temperatures (T_g) of the cured products are given in Table I. The diglycidyl ether of TBTMBP had the highest T_g , which was 225°C.

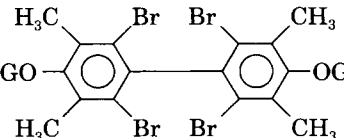
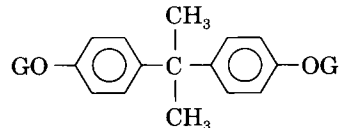
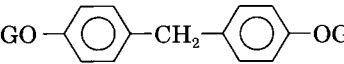
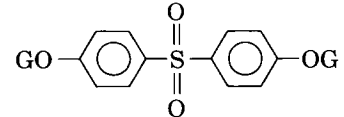
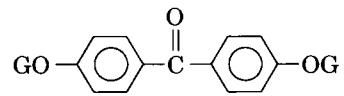
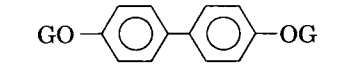
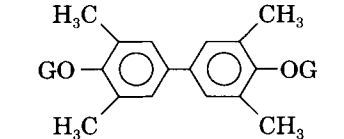
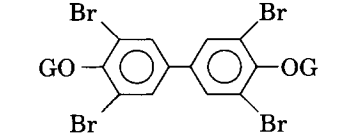
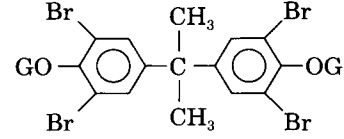
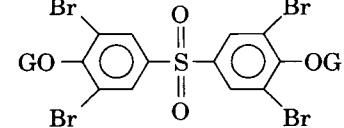
High Thermal Stability of TBTMBP Epoxy Resins

The same curing procedure as described above was applied in this case, except that diaminodiphenyl sulfone was used as a curing agent instead of methylenedianiline. The amounts of epoxy resins, curing agent, and the dynamic decomposition temperatures of the cured products are listed in Table II. The dynamic decomposition temperature was determined by heating the sample at a rate of 3°C/min and by observing the onset of degradation (observed by a weight loss). The diglycidyl ether of TBTMBP had the highest dynamic decomposition temperature of 230°C, which was at least 50°C higher than the conventional ortho-brominated epoxy resins.

Retention of Flexural Strength

Various epoxy resins were mixed with methylenedianiline at 150°C, poured into a hot aluminum mold, cured in an oven at 175°C for 1 h, post-cured at 200°C for 1 h, and finally were postcured at 230°C for 30 min. The amounts of epoxy resins, curing agent, and the flexural strength of the cured products are shown in Table III. At 210°C, the diglycidyl ether of TBTMBP retains 61% of the original flexural strength as compared with 23% retention for the TBBA.

Table I Glass Transition Temperature (T_g)

| Epoxies (G = CH ₂ -CH(O)-CH ₂) | Resin (g/eq) | Curing Agent (g/eq) | T_g (°C) |
|---|--------------|---------------------|------------|
|  | 50/0.137 | 6.7/0.135 | 225 |
|  | 50/0.269 | 13.3/0.269 | 165 |
|  | 50/0.294 | 14.6/0.295 | 150 |
|  | 50/0.256 | 12.7/0.257 | 190 |
|  | 50/0.281 | 13.9/0.281 | 185 |
|  | 50/0.303 | 15.0/0.303 | 191 |
|  | 50/0.265 | 13.1/0.265 | 205 |
|  | 50/0.143 | 7.1/0.143 | 210 |
|  | 50/0.154 | 7.6/0.154 | 200 |
|  | 50/0.142 | 7.0/0.141 | 186 |

Hydrolytic Stability

The sample was dissolved in 1,4-dioxane and saponified by refluxing with 3N ethanoic KOH solu-

tion. The resulting halides were titrated with standard silver nitrate solution. From the volume of titrant used, hydrolyzable chloride and hydrolyzable bromide are calculated. The results in Table IV

Table II Thermal Stability

| Epoxyes (G = CH ₂ -CH-CH ₂) | Resin (g/eq) | Curing Agent (g/eq) | Dyn. Decomp. Temp. (°C) |
|--|--------------|---------------------|-------------------------|
| | 50/0.137 | 8.4/0.136 | 320 |
| | 50/0.143 | 9.8/0.144 | 270 |
| | 50/0.154 | 9.5/0.153 | 268 |
| | 50/0.142 | 8.8/0.142 | 255 |

demonstrate the superior hydrolytic stability of meta-brominated epoxy resin over the ortho-brominated epoxy resin.

RESULTS AND DISCUSSION

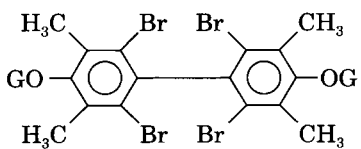
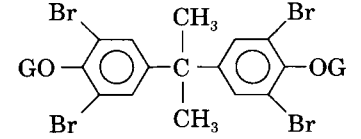
It has been reported by one of the authors⁹⁻¹⁰ that the ortho- or para-brominated phenol forms an un-

stable cyclohexadienone structure via keto-enol tautomerization. Upon heating, this unstable cyclohexadienone structure generates bromine radicals, which, in turn, abstract a proton from neighboring molecules to form HBr. Meta-brominated phenolics will not generate bromine radicals as readily as ortho- or para-brominated phenol because of the location of bromine. This proposition was further demonstrated by the electron spin resonance (ESR) measurement of the free radical concentra-

Table III Retention of Flexural Strength

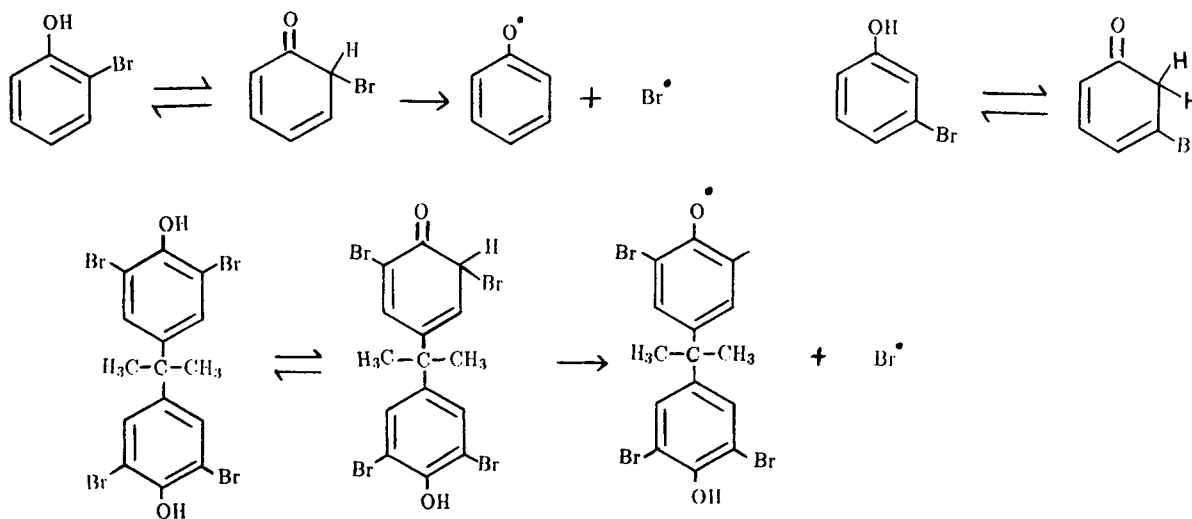
| Epoxyes | Resin (g/eq) | Curing Agent (g/eq) | Flexural Strength, psi | | | % Retention | |
|---------|--------------|---------------------|------------------------|-------|-------|-------------|-------|
| | | | 25°C | 180°C | 210°C | 180°C | 210°C |
| | 150/0.411 | 20.4/0.408 | 13,000 | 9279 | 7866 | 71 | 61 |
| | 150/0.462 | 28.5/0.459 | 13,500 | 5150 | 3105 | 38 | 23 |

Table IV Hydrolytic Stability: Total Hydrolyzable Halide Analysis

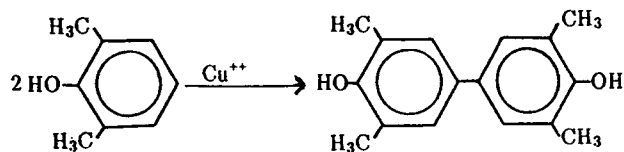
| Epoxies | Hydrolyzable Chloride (ppm) | Hydrolyzable Bromide (ppm) |
|---|-----------------------------|----------------------------|
|  | 48 | 0 |
|  | 45 | 180 |

tions of ortho-brominated tetrabromobisphenol-A (TBBA) and the meta-brominated 2,4,6-trimethyl-

phenol after heating at 250°C for 1 h. A relative radical concentration of 960 for TBBA to <10 for the meta-brominated trimethylphenol was observed.

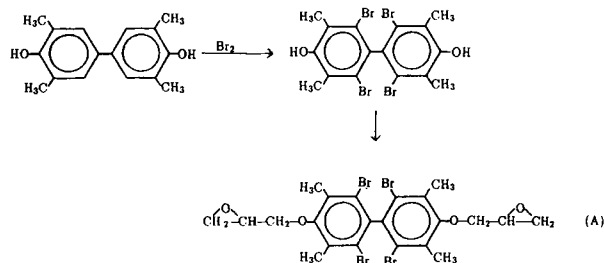


In order to brominate a biphenol at the meta positions the ortho positions have to be blocked first. The starting 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP obtained from Mitsubishi Petrochemical Company) was produced by the oxidative dimerization of 2,6-dimethylphenol using cupric salt as a catalyst.¹¹



Bromination of TMBP with excess bromine at 40°C without catalyst in methylene chloride produces a mixture of 4% tribromo- and 96% tetra-

bromo-compounds. Further purification from acetone yields better than 98% purity TBTMBP, which is then epoxidized to the corresponding diglycidyl ether.



In view of the extraordinary thermal and hydrolytic stability exhibited by the diglycidyl ether of

TBTMBP, its applications for the electronic packaging and printed circuit board were evaluated.

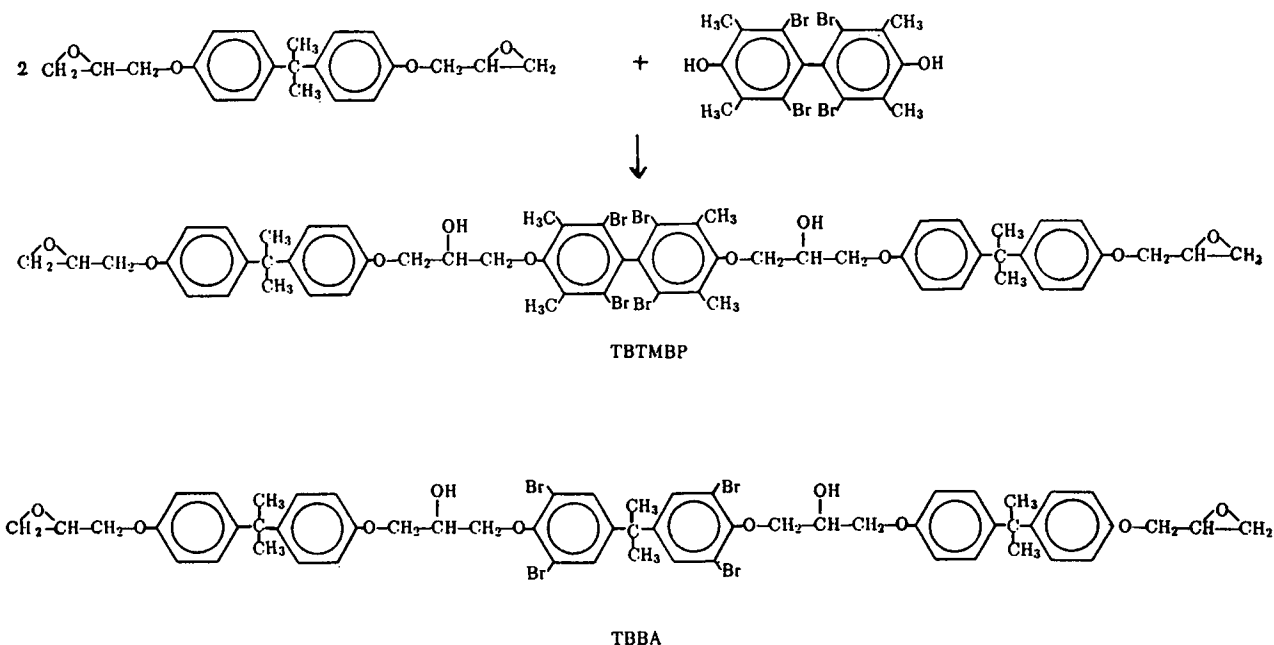
Electronic Encapsulation Application

Encapsulation Formulation

The diglycidyl ethers of TBTMBP and TBBA are separately blended with standard cresol formaldehyde novolac epoxy resin (CNE) to form encapsulation formulations having a bromine content of 1.25%. The control resin is designated for the mixture of Quatrex 3430 (a CNE, the Dow Chemical Company) and Quatrex 6410 (ortho-brominated epoxy resin of TBBA, the Dow Chemical Company). The formulations are each cured at 175°C for 4 h. Encapsulation formulations are given in Table V.

Flame Retardancy Test

Both formulations passed UL-94 VO flame retardancy test using a 1/16 inch thickness casting.



Laminating varnishes were prepared by blending the advanced epoxy resins made from TBTMBP and TBBA with solvent, dicyandiamide and 2-methylimidazole catalyst. Burlington style 7628 glass cloth was impregnated with the above-prepared laminating varnish in a forced air vertical treater heated to 175°C. Eight 12 in. × 12 in. piles were pressed at 175°C for 60 min at a pressure of 500 psig.

Laminate varnish compositions and test results are shown in Table VII. The laminate board made

Device Reliability Test

The device was tested by a highly accelerated stress test which involved the following conditions: 121°C, 15 psig steam, and 25 V bias. The device used was a 14-pin LM 324 quad operational amplifier with a single passivation layer. The percentage of devices that fail, as a function of time, is given in Table VI. The results in Table VI clearly demonstrate the superior performance of the meta-brominated epoxy resin, which extends the life of the device many times more than the ordinary epoxy resin.

Electrical Laminate Application

Advanced epoxy resins containing bromine atoms are particularly useful in circuit boards and other electrical laminate applications. These types of epoxy resins are prepared by reacting an epoxy resin (DGE of Bisphenol-A) with a polyhydric phenol that contains bromine atoms. The advanced epoxy resins made from TBTMBP and TBBA are as follows:

from the advanced epoxy resin of TBTMBP has a T_g of 155°C and has passed the Blister Resistance test 100%, as compared with a T_g of 120°C and 0% pass for the board made from the advanced epoxy resin of TBBA.

CONCLUSION

Meta-halogenated phenols are generally known to be more chemically and thermally stable than their

Table V Encapsulation Formulation

| Component | Control | A |
|--------------------------|-----------------------|-------------------------|
| Brominated Resin (g) | 25.6 (DGE of TBBA) | 26.3 (DGE of TBTMBP) |
| CNE (g) | 174.4 | 173.7 |
| Curing Agent (g) | 89.5 | 89.5 |
| Triphenyl Phosphine (g) | 2.25 | 2.25 |
| Mold Release Agent (g) | 4.0 | 4.0 |
| Epoxy Silane (g) | 4.0 | 4.0 |
| Fused Silica (g) | 685.0 | 685.0 |
| Antimony Oxide (g) | 10.0 | 10.0 |
| Carbon Black (g) | 4.0 | 4.0 |
| % Bromine in Formulation | 1.25 | 1.25 |

The curing agent is a phenol-formaldehyde novolac resin with an average hydroxyl functionality of 6 and a phenolic hydroxyl equiv. wt. of 104. (Schenectady Chemical).

The mold release agent is a refined Montan wax from Hoechst.

The epoxy silane is Z-6040, available from Dow Corning Corp.

ortho- or para-halogenated counterparts. Novel 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol and its epoxy derivatives are synthesized to incorporate this stable meta-bromophenol moiety into epoxy resin systems. In semiconductor encapsulation and laminate board applications, epoxy systems derived from TBTMBP have exhibited su-

perior hydrolytic and thermal stability as compared with the conventional ortho-brominated epoxy resins. These properties have resulted in an extended device life for semiconductors and a high T_g with excellent blister resistance for printed circuit boards, while at the same time providing the required flame retardancy.

Table VI Device Reliability

| Sample Number | % Device Failure | | |
|---------------|------------------|-------|-------|
| | 400 h | 600 h | 800 h |
| Control | 25 | 75 | 100 |
| A | 0 | 2 | 13 |

Table VII Laminate Varnish Composition and Testing Results

| | TBTMBP | TBBA |
|--|--------|------|
| Advanced Epoxy Resin (g) | 3200 | 3200 |
| Acetone (g) | 1464 | 1814 |
| Dimethylformamide (g) | 493 | 493 |
| Monomethyl Ether of Propylene Glycol (g) | 432 | 432 |
| Dicyandiamide (g) | 96 | 96 |
| 2-Methylimidazole (g) | 3.2 | 3.2 |
| Gel Time of Prepreg (171°C/s) | 70 | 90 |
| T_g (°C) | 155 | 120 |
| Blister Resistance Test (% pass) | 100 | 0 |

REFERENCES

1. M. M. Khan and H. Fatemi, *Proc. Int. Symp. Microel.*, **9**, 420 (1986).
2. S. Ahmad, R. Blish, T. Corbett, J. King, and G. Shirley, *Comp. Hybr. Manuf. Technol.*, **9**(4), 379 (1986).
3. R. J. Gale, *Proc. IEEE Int. Rel. Phys. Symp.*, 37 (1984).
4. K. N. Ritz, W. T. Stacey, and E. K. Broadbent, *Proc. IEEE Int. Rel. Phys. Symp.*, 28 (1987).
5. M. M. Khan, H. Fatemi, J. Romero, and E. Delenia, *Proc. IEEE Int. Rel. Phys. Symp.*, 40 (1988).
6. A. Factor, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1691 (1973).
7. S. Nara and K. Matsuyama, *J. Macromol. Sci. Chem.*, **A5**, 1205 (1971).
8. Y. Zaks, J. Lo, D. Raucher, and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**, 913 (1982).
9. C. S. Wang, D. B. Fritz, and A. Mendoza, *ACS Symposium*, **407**, 397 (1988).
10. D. B. Fritz and C. S. Wang, *ACS Symposium*, **407**, 405 (1988).
11. M. Imanari, H. Iwane, and T. Sugawara, U.S. Patent 4 564 713 (1986); Jap. Kokai Tokkyo Koho 61-268641 (1986).

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