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# Synthesis of aromatic diamino-functionalized dimethylsiloxane oligomers and macromonomers

**Yusuke Kawakami*, Shan-Pu Yu, and Toshihiro Abe**

Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa,
Nagoya 464 Japan

## Summary

Methods to synthesize dimethylsiloxane oligomers and macromonomers with aromatic diamino function were studied. Telechelic oligomers having 4-aminophenyl groups on both ends of the molecule(**1**) were synthesized by the reaction of 4-[*N,N*-bis(trimethylsilyl)amino]phenyllithium with α,ω-dichlorooligodimethylsiloxane. Reaction of the lithium reagent with methyltrichlorosilane followed by methanolysis and successive hydrolysis gave methylbis(4-aminophenyl)silanol. Reaction of the silanol with oligodimethylsiloxane with mono-dimethylchlorosilyl function at one end of the molecule gave dimethylsiloxane oligomers having methylbis(4-aminophenyl)silyl function at one end of the molecule(**2**).

Protection of the amino groups of bis(4-aminophenyl)methane as bis(trimethylsilyl)amino group, metalation of methylene group by butyllithium-*N,N,N',N'*-tetramethylethylenediamine (TMEDA), followed by the reaction with mono-dimethylchlorosilyl-functionalized oligodimethylsiloxanes gave oligodimethylsiloxanes having bis(4-aminophenyl)methyl function at one end of the molecule(**3**).

Polydimethylsiloxane macromonomers having bis(4-aminophenyl)methyl function were obtained by end-capping the living end of the polymerization of hexamethylcyclotrisiloxane($D_3$) by lithium bis[4-{bis(trimethylsilyl)amino}phenyl]methide with trimethylchlorosilane and removal of the protecting group.

## Introduction

We already reported methods to synthesize vinyl-polymerizable polydimethylsiloxane macromonomer(1) and terminal dicarboxylic- or diol-functionalized macromonomers for polyaddition reaction(2). Physical property of a backbone polymer is changed by the introduction of oligo- or polydimethylsiloxane component into the polymer by homopolymerization or copolymerization of such macromonomers. For example, introduction of oligodimethylsiloxane as *p*-substituents into polystyrene backbone was shown to be an excellent method to develop selectively oxygen permeable membrane materials of well-balanced property between mechanical strength, permeability and selectivity in permeation(3-8). Polydimethylsiloxane introduced into vinyl polymers as long branches are quite effective to modify surface properties of the backbone polymers(9, 10). Poly(methyl methacrylate) component in polyamide or polyurethane can combine the properties of polyamide or polyurethane and poly(methyl methacrylate)(11).

It is of interest to study the effect of siloxane component on hydrogen bonding and on the mechanical strength of the polycondensation type polymers. Although, there is already a report in which polydimethylsiloxane was introduced into polyamide as a block(12, 13), no report was seen about the graft polymers having oligo- or polydimethylsiloxane branches of well-controlled length and structure.

In this communication, we would like to report the methods of the synthesis of oligo- or polydimethylsiloxane telechelics(**1**) and macromonomers(**2**,**3**) of well-controlled molecular weight and molecular weight distribution which will give well-controlled structure of polycondensation type graft polymers with siloxane component, or polymers with short dimethylsiloxane chains distributed homogeneously in the molecule.

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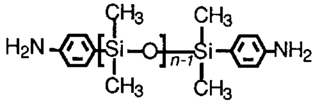
*Corresponding author, present address: Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Hokuriku, Asahidai 15, Tatsunokuchi, Ishikawa 923-12 Japan



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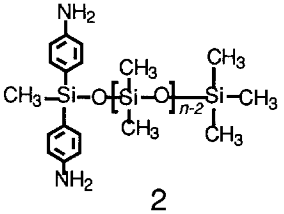

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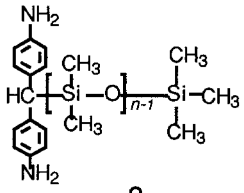

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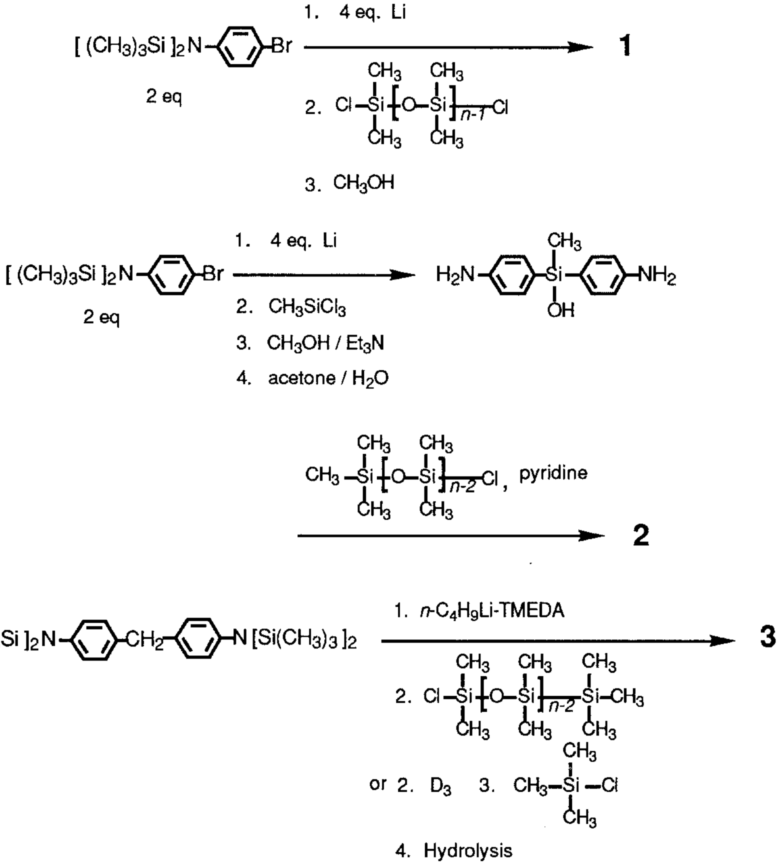
## Experimental

### Synthetic Scheme



### Separation and Analysis

Thin layer and column chromatography were carried out on silica gel. Proton NMR spectra were recorded in $CDCl_3$ or dimethylsulfoxide-$d_6$ on a Varian 200 MHz spectrometer model Gemini 200. Number average molecular weight was estimated by titration and NMR spectroscopy. The molecular weight was also estimated by a Corona vapor phase osmometer, model 114. Molecular weight distribution was evaluated by GPC.

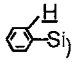
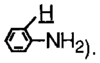
### Synthetic Procedure

Protection of amino function as bis(trimethylsilyl)amino group was carried out as reported(14).

### *Synthesis of 1*

Bis(4-aminophenyl)dimethylsilane(n=1)

To lithium powder(0.39 g, 56 mmole) and ether(5 $cm^3$) in an argon-purged 50 $cm^3$ flask, *N,N*-bis(trimethylsilyl)-4-bromoaniline(6.60 g, 38 mmole) in ether(10 $cm^3$) was added dropwise during 2 h, and further reacted for 3 h at room temperature. To this solution dimethyldichlorosilane(0.97 g, 7.5 mmole) in ether(5 $cm^3$) was added dropwise during 1 h at 0 °C, and further allowed to react for 12 h at room temperature. After evaporation of ether, hexane(50 $cm^3$) was added, and formed salt was removed by filtration. Methanol(50 $cm^3$) was added to the residual material after evaporation of hexane, and the solution was stirred overnight. The crude product obtained by evaporation of the solvent was purified by column chromatography. Rf=0.25(eluent; ether:hexane=3:1). Yield 76 %.

Chemical shifts: 0.43(s, 6H, $Si(C\underline{H}_3)_2$) , 3.7(broad s, 4H, $N\underline{H}_2$), 6.66(d, 4H, J=8.4 Hz, ),
7.29(d, 4H, J=8.4 Hz, ).

1,3-Bis(4-aminophenyl)tetramethyldisiloxane(n=2)

1,3-Dichlorotetramethyldisiloxane was used in the synthesis. Similar treatment in the case of the synthesis of bis(4-aminophenyl)dimethylsilane gave the product. Rf=0.3(eluent; ether: hexane=4:1). Yield 77 %.
Chemical shift: 0.24(s, 12H, $Si(C\underline{H}_3)_2$).

1,5-Bis(4-aminophenyl)hexamethyltrisiloxane(n=3)

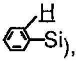
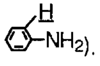
1,5-Dichlorohexamethyltrisiloxane was used. Concentration of 4-[*N,N*-bis(trimethylsilyl)-amino]phenyllithium was half of that in the case of the synthesis of 1,3-bis(4-aminophenyl)tetramethyldisiloxane. Temperature was maintained at -78°C during the addition of the reagent. Rf=0.3(eluent; ether: hexane=4:1). Yield 53 %.
Chemical shifts: - 0.01(s, 6H, $OSi(C\underline{H}_3)_2O$), 0.25(s, 12H, $CSi(C\underline{H}_3)_2O$) .

1,7-Bis(4-aminophenyl)octramethyltetrasiloxane(n=4)
Rf=0.3(eluent; ether: hexane=4:1). Yield 40 %.
Chemical shifts: 0.00(s, 12H, $OSi(C\underline{H}_3)_2O$), 0.27(s, 12H, $CSi(C\underline{H}_3)_2O$).

Amino and aromatic protons of 1,3-bis(4-aminophenyl)tetramethyldisiloxane, 1,5-bis(4-aminophenyl)hexamethyltrisiloxane and 1,7-bis(4-aminophenyl)octramethyltetrasiloxane were observed at similar positions with bis(4-aminophenyl)dimethylsilane.

### *Synthesis of 2*

Methylmethoxybis(4-aminophenyl)sillane

To a solution of 4-[*N,N*-bis(trimethylsilyl)amino]phenyllithium prepared from lithium powder(0.24 g, 35 mmole) and *N,N*-bis(trimethylsilyl)-4-bromoaniline(5.06 g, 16 mmol) in ether(15 $cm^3$) at dry-ice temperature, methyltrichlorosilane(1.08 g, 7.1 mmole) in ether(5 $cm^3$) was added all at once. The reaction system was allowed to warm-up to room temperature, and further reacted for 12 h at the temperature. After evaporation of ether, hexane(50 $cm^3$) was added to the residue, and formed solid and unreacted lithium was removed by filtration. Evaporation of hexane gave crude product. To this oily crude product, methanol(100 $cm^3$) and triethylamine(10 $cm^3$) were added, and the mixture was further stirred for overnight. After removal of methanol, the pure product was isolated by column chromatography. Rf=0.3(eluent; ether:hexane=4:1). Yield 57 %.
Chemical shifts: 0.51(s, 3H, $SiC\underline{H}_3$), 3.46(s, 3H, $OC\underline{H}_3$), 3.73(broad s, 4H, $N\underline{H}_2$) , 6.67(d, 4H, J=8.2 Hz, ), 7.36(d, 4H, J=8.2 Hz, ).

Methylbis(4-aminophenyl)sillanol

Methylmethoxybis(4-aminophenyl)sillane(0.90 g, 3.5 mmole) was dissolved in acetone(20 $cm^3$) and water(20 $cm^3$), and the reaction system was heated to reflux for overnight. After cooling to room temperature the reaction system was extracted with chloroform(three times, 10 $cm^3$ each).

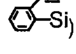
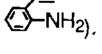
Crude product obtained by the evaporation of the solvent was purified by column chromatography. Rf=0.2(eluent; ether:hexane=5:1). Yield 82 %.

This compound was used for further reaction immediately after the separation.

1,1-Bis(4-aminophenyl)tetramethyldisiloxane(n=2)

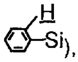
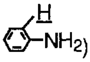
Methylbis(4-aminophenyl)sillanol(0.31 g, 1.3 mmole) was dissolved in ether(20 $cm^3$), pyridine(0.74 g, 9.4 mmole) and trimethylchlorosilane(1.6 g, 14.7 mmole) were added, and the reaction system was kept at room temperature overnight under stirring. After the volatile material was removed by evaporation, water(10 $cm^3$) was added to the residual material and extracted three times with ether(20 $cm^3$ each). The product was isolated by column chromatography after the removal of the solvent.

Rf=0.4(eluent; ether:hexane=4:1). Yield 78 %.

Chemical shifts: 0.04(s, 9H, $Si(C\underline{H}_3)_3$), 0.46(s, 3H, $SiC\underline{H}_3$), 3.7(broad s, 4H, $N\underline{H}_2$) , 6.65(d, 4H, J=8.2 Hz, ), 7.31(d, 4H, J=8.2 Hz, ).

1,1-Bis(4-aminophenyl)hexamethyltrisiloxane(n=3)

Rf=0.4(eluent; ether:hexane=4:1). Yield 70 %.

Chemical shifts: -0.01(s, 6H, $OSi(C\underline{H}_3)_2O$), 0.02(s, 9H, $Si(C\underline{H}_3)_3$), 0.45(s, 3H, $SiC\underline{H}_3$), 3.7(broad s, 4H, $N\underline{H}_2$), 6.65(d, 4H, J=8.2 Hz, ), 7.31(d, 4H, J=8.2 Hz, ).

### *Metalation of bis[4-{bis(trimethylsilyl)amino}phenyl]methane*

To dry hexane(4 $cm^3$) solution of bis[4-{bis(trimethylsilyl)amino}phenyl]methane(2.59 g, 5.31 mmol) and TMEDA(0.65 g, 5.57 mmol), hexane solution of *n*- butyllithium (1.58 mol/L, 3.39 $cm^3$ , 5.36 mmol) was added dropwise at room temperature(15). The reaction system became red during stirring at room temperature, which indicates the formation of carbanion.

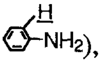
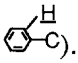
The reaction was stopped with deuterium oxide, and extent of metalation was estimated by the amounts of deuterium incorporated into the methylene group of bis(4-aminophenyl)methane.

### *Synthesis of 3*

Bis(4-aminophenyl)methyltrimethylsilane(n=1)

To a nitrogen-purged 300 $cm^3$ flask, bis[4-{bis(trimethylsilyl)amino}phenyl}]methane(47.5 g, 0.10 mole), TMEDA(12.9 g, 0.11 mole) and hexane solution of *n*-butyllithium(1.58 mol/L, 70 $cm^3$, 0.11 mole) were added successively in this order at room temperature. After kept for 4 h at ambient temperature, the reaction system was added from a dropping funnel to trimethylchlorosilane(24.7 $cm^3$, 0.19 mole) in hexane(100 $cm^3$) at 0° C during 0.5 h, and allowed to react overnight. After the removal of the volatile material, hexane (50 $cm^3$) was added, and formed salt was removed by filtration. The hexane solution was evaporated to give an oil. Ether(200 $cm^3$) and glacial acetic acid(24.0 g, 0.40 mole) was added to the system, stirred overnight at room temperature, and water (100 $cm^3$) was added. The separated ether solution was extracted with water(three times, 100 $cm^3$ each) to remove the acetic acid, and dried over magnesium sulfate. Evaporation of the solvent gave crude product. Pure product was isolated by column chromatography.

Rf=0.3(eluent; ether:hexane= 4:1). Yield 44 %.

Chemical shifts: - 0.02(s, 9H, $SiC\underline{H}_3$), 3.25(s, 1H, $C\underline{H}$), 3.5(broad s, 4H, $N\underline{H}_2$), 6.63(d, 4H, J=6.4 Hz, ), 6.97(d, 4H, J=6.4 Hz, ).

Bis(4-aminophenyl)methylpentamethyldisiloxane(n=2)

After the metalation procedure, the solution was added into the hexane solution of pentamethylchlorodisiloxane, and the reaction product was isolated similarly. Rf=0.3(eluent; ether:hexane= 5:2). Yield 56 %.

Chemical shifts: - 0.03(s, 9H, $Si(C\underline{H}_3)_3$), 0.00(s, 6H, $CHSi(C\underline{H}_3)_2$), 3.20(s, 1H, $C\underline{H}$), 3.48(broad s, 4H, $N\underline{H}_2$). Aromatic protons appeared at similar positions with bis(4-aminophenyl)methyltrimethylsilane.

1-[Bis(4-aminophenyl)methyl]heptamethyltrisiloxane(n=3)
Rf=0.3(eluent; ether:hexane= 5:2). Yield 52 %.
Chemical shifts: - 0.08(s, 9H, Si($C\underline{H}_3$)$_3$), 0.02(s, 6H, OSi($C\underline{H}_3$)$_2$O), 0.05(s, 6H, CHSi($C\underline{H}_3$)$_2$). Methine, amino and aromatic protons appeared at similar positions with [bis(4-aminophenyl)-methyl]pentamethyldisiloxane.

1-[Bis(4-aminophenyl)methyl]polydimethylsiloxane macromonomer
Polydimethylsiloxane macromonomer was synthesized by stopping the living polymerization of hexamethylcyclotrisiloxane(D3) initiated by lithium bis[4-bis(trimethylsilyl)aminophenyl]methide with trimethylchlorosilane.

These compounds were also synthesized as follows: The solution of lithium bis[4-{bis(trimethylsilyl)amino}phenyl]methide(0.22 mole) prepared in the synthesis of bis(4-aminophenyl)methyltrimethylsilane was added dropwise into the solution of 1,3-dichlorotetramethyldisiloxane(23.3 g, 0.24 mole in hexane 200 cm$^3$) at 0 °C. After the reaction system was kept overnight, methyllithium(0.12 mole) was added to the system at 0 °C. After the reaction system was kept for 3 h, trimethylchlorosilane(18.2 cm$^3$, 0.14 mole) was added to the reaction system. After the removal of the volatile materials, the reaction product was treated similarly to the case of the synthesis of the compound from 1-chloroheptamethyltrisiloxane.

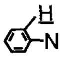
## Results and Discussion

The temperature of the addition of the reagent should be kept at -78°C in the synthesis of telechelic aminophenyl-functionalized oligodimethylsiloxane **1** having three silicon atoms or more(longer than trisiloxane) in order to avoid the scission of the siloxane linkage.

In the synthesis of methylbis(4-aminophenyl)sillanol to prepare **2**, the reaction product methylbis[4-{bis(trimethylsilyl)amino}phenyl]chlorosilane was hydrolyzed in two steps, first by methanol/triethylamine to methylmethoxybis(4-aminophenyl)silane and second by acetone/water to methylbis(4-aminophenyl)silanol. This procedure is necessary because direct hydrolysis of the crude methylbis[4-{bis(trimethylsilyl)amino}phenyl]chlorosilane by water gave 1,1-bis(4-aminophenyl)tetramethyldisiloxane as a condensation product. Methylmethoxybis(4-aminophenyl)sillane can be hydrolyzed to silanol by the treatment with water in acetone without condensation. However, since the silanol is easy to condense to the dimer or turn into unidentified compound, it should be used for further reaction as soon as possible after the isolation. Protection of amino group is essential in the synthesis. Protection of amino group as 1-aza-2,5-bis(dimethylsila)cylopentyl group is sometimes suitable(16).

Metalation of bis[4-{bis(trimethylsilyl)amino}phenyl]methane to synthesize **3** proceeded nicely in hexane, but did not proceed in other solvents like ether or tetrahydrofuran. The extent of the metalation was estimated by the decrease of the methylene proton signal in $^1$H NMR spectroscopy. Concentration of the reagents ia very important to attain high conversion in metalation. Seventy percent of the methylene proton was metalated in the reaction of the concentration of the reagents being 0.5 mol/L at 25°C for 5h. Lowering the concentration resulted in lower conversion in metalation.

In the addition of chlorosiloxane, the reaction conditions are very important to obtain the desired mono-silylated product in good yield. Lithium bis[4-bis(trimethylsilyl)aminophenyl]methide was added to the solution of 1-chlorooligodimethylsiloxane during proper time. The reaction temperature should not be elevated above 0°C by the liberated heat in order to avoid double silylation reaction via metalation of the mono-silylated product.

In the synthesis of **3** by the reaction of lithium bis[4-bis(trimethylsilyl)aminophenyl]methide with $\alpha,\omega$-dichlorooligodimethylsiloxane and end-capping of the remaining chlorosilyl function with methyllithium, following cautions must be taken in addition to the above-mentioned cautions. The lithium reagent should be added into the solution of excess $\alpha,\omega$-dichlorooligodimethylsiloxane. If the addition is too fast, bis-functionalized oligodimethyl-siloxane by lithium bis[{4-bis(trimethylsilyl)amino}phenyl]methide was formed. Removal of liberated TMEDA at the mono-silylation step before the end-capping reaction with methyllithium is also essential to avoid unnecessary metalation of remaining methine group by newly formed methyllithium-TMEDA complex from remaining methyllithium and liberated TMEDA. If such double metalation occurs, for example in the synthesis of **3**(n=1), two trimethylsilyl groups are attached to the central benzylic carbon, whose characteristic NMR spectra are assigned to the peaks appeared at around 0.08( s, CSi($C\underline{H}_3$)$_3$), -0.09( s, 9H, Si($C\underline{H}_3$)$_3$), and 6.64(d, -NH$_2$). Trimethylchlorosilane was added to terminate the reaction.

Since there were multi components in the crude product, the isolated yield became rather low, 29 % for 1-[bis(4-aminophenyl)methyl]heptamethyltrisiloxane. It is better to use 1-chlorononamethyl-tetrasiloxane or $D_3$ and trimethylchlorosilane as capping agent in the synthesis of 1-[bis(4-aminophenyl)methyl]nonamethyltetrasiloxane in order to avoid the unnecessary double metalation of the methine group.

Removal of the protecting group by hydrolysis in the presence of acetic acid gave the product in good yield. Deprotection of the trimethylsilyl group can be also carried out by the repeated treatment with methanol after complete removal of the formed solid by passing through short path silica gel column.

Macromonomers were prepared by initiating the polymerization of $D_3$ by lithium bis[4-bis(trimethylsilyl)aminophenyl]methide and stopping the reaction with trimethylchlorosilane. The results of the synthesis of macromonomers are shown in Table 1.

Table 1. Molecular Weight Data of Macromonomers

| [M] / [ I ]a) | Yield(%)b) | *Mn*,calc | *Mn*,VPO | *Mn*,titc) | *Mn*,NMR | *Mn*,GPCd) | *Mw* / *Mn* |
|---|---|---|---|---|---|---|---|
| 19 | 81 | 5600 | 5100 | 8300 | 7700 | 6300 | 1.3 |
| 38 | 79 | 11000 | 12000 | 17000 | 17000 | 14000 | 1.5 |

a) THF solution of monomer, [M]=0.6 mol / l was added to hexane solution of initiator, [ I ]=0.8 mol /l at 25°C. Reaction time, 24hr.
b) Methanol insoluble fraction.
c) Estimated by the titration of amino group.
d) Eestimated by GPC using polystyrene as standard.

The calculated and experimental values by VPO are in good accordance, which indicates that all the lithium reagents are used to initiate the polymerization. It was shown, by separate experiments, that both *n*-butylithium and *n*-butylithium-TMEDA system can polymerize $D_3$ at almost same rate with that by ithium bis[4-bis(trimethylsilyl)aminophenyl]methide-TMEDA system. The higher experimental value of *Mn* by NMR and titration indicates that the polymerization product contains not only the desired amino-functionalized polydimethylsiloxane macromonomer but also unfunctionalized polydimethylsiloxane initiated by *n*-butyllithium or *n*-butylithium-TMEDA system. The calculated value is about 70 % of that of experimental value which is in goood accordance with the percent of the metalation of bis[4-bis(trimethylsilyl)aminophenyl]methane. Since the property of the functionalized macromonomer and unfunctionalized polydimethylsiloxane is similar, it is difficult to separate unfunctionalized polydimethylsiloxane from the macromonomer.

## Acknowledgments

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## References

1. Y. Kawakami, Y. Miki, T. Tsuda, R. A. N. Murthy, Y. Yamashita(1983) Polym. J. **14**: 913
2. Y. Kawakami, S. Saibara, F. Suzuki, T. Abe, Y. Yamashita(1991) Polym. Bull. **25**: 521
3. Y. Kawakami, T. Aoki, H. Hisada, Y. Yamamura, Y. Yamashita(1985) Polym. Comm. **26**: 133
4. Y. Kawakami, H. Karasawa, T. Aoki, Y. Yamamura, H. Hisada, Y. Yamashita(1985) Polym. J. **17**: 1159
5. Y. Kawakami, H. Karasawa, H. Kamiya, T. Aoki, Y. Yamashita(1986) Polym. J. **18**: 237
6. Y. Kawakami, H. Toda, M. Higashino, Y. Yamashita(1988) Polym. J. **20**: 285
7. Y. Kawakami, T. Sugisaka, Y. Yamashita(1988) Polym. J. **20**: 685
8. Y. Kawakami, T. Sugisaka(1990) J. Memb. Sci. **50**: 189
9. Y. Kawakami, Y. Miki, T. Tsuda, R. A. N. Murthy, Y. Yamashita((1983) Polym. J. **14**: 913
10. Y. Kawakami, R. A. N. Murthy, Y. Yamashita((1984) Makromol. Chem. **185**: 9
11. Y. Yamashita, Y. Chujo, H. Kobayashi, Y. Kawakami(1981) Polym. Bull. **5**: 361
12. M. Kajiyama, Y. Nishikata, M. Kakimoto, Y. Imai(1986) Polym. J. **18**: 735
13. M. Kakimoto, M. Kajiyama, Y. Imai(1986) Polym. J. **18**: 935
14. R. B. Weisenfeld(1986) J. Org. Chem. Soc. **51**: 2434
15. A. W. Langer, Jr(May 16, 1972) US 3,663,585
16. S. Djuric, J. Venit, P. Magnus(1981) Tetrahedron Lett. **22**:1787

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