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Synthesis of dicarboxylic acid functionalized polysiloxane macromers

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Summary

Methods to synthesize aliphatic and aromatic dicarboxylic acid functionalized polydimethylsiloxane macromers were studied. Introduction of allyl group into dicarboxylic acid as a substituent, followed by hydrosilylation by silane terminated polydimethylsiloxane was found satisfactory to obtain the macromers.

Introduction

We already reported methods to synthesize vinyl-polymerizable polydimethylsiloxane macromer(1) and terminal bifunctionally functionalized macromer for polyaddition reaction(2).

Introduction of oligo- or polydimethylsiloxane component into vinyl polymers by copolymerization or homopolymerization of such macromer changes the physical property of the polymers. For example, introduction of oligodimethylsiloxane as substituents into polymer backbone was shown to be an excellent method to develop selectively oxygen permeable membrane materials of well-balanced property between mechanical strength and selectivity in permeation(3-6). Introduction of vinyl-polymerizable poly(methyl methacrylate) macromer into polyamide can combine the properties of polyamide and poly(methyl methacrylate)(2). 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(7), no report was seen about the graft polymers of well-controlled structure.

In this communication, we would like to report the method of the synthesis of oligo- or polydimethylsiloxane macromers of well-controlled molecular weight and molecular weight distribution which will give well-controlled structure of polycondensation type graft polymers with siloxane component.

Experimental

NMR Spectra

NMR spectra were recorded on a Varian 200 MHz spectrometer model Gemini 200.

Dicarboxylic Compounds

Introduction of allylic group to dicarboxylic acids which will be put at the end of polydimethylsiloxane were synthesized according to Scheme 1. After the reaction, carboxylic groups were protected as silyl ester.

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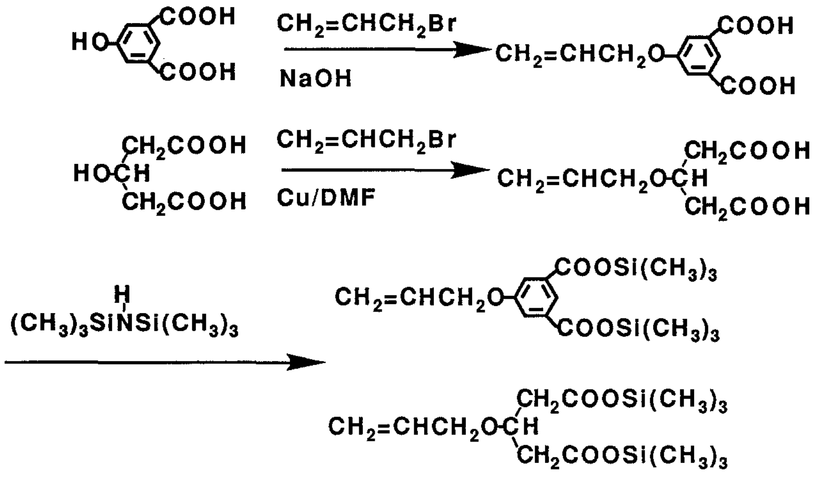


Scheme 1. Synthesis of Allyl Functionalized Dicarboxylic Compounds for Hydrosilylation

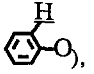
5-Allyloxyisophthalic acid

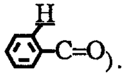
This compound was synthesized by three different procedures. i) First protection of carboxylic group as ethyl ester followed by allylation and hydrolysis, ii) reaction of both phenol and carboxylic functions with allyl bromide followed by hydrolysis, iii) selective allylation of phenol function.

i) Diethyl 5-hydroxyisophthalate(0.478 g, 1.92 mmol) synthesized from the acid in the presence of 1,8-diazabicyclo[5.4.0]undecene(8), was converted into allyl ether by the reaction of the sodium salt with excess allyl bromide in dimethylformamide(DMF)(20 ml) at 0°C. B.p. 170~180°C(0.15 mmHg). Yield 0.51 g, 95%. Hydrolysis of the ester(2.08 g, 7.5 mmol) with potassium hydroxide(1.3 g, 72.8 mmol) in ethanol(20 ml), followed by acidification with dilute hydrochloric acid gave 1.53 g of the acid. The crude product was recrystallized from water. Yield 93%. M.p. 175°C.

ii) 5-Hydroxyisophthalic acid(6.03 g, 32.1 mmol) was converted into potassium salt by the reaction with potassium hydroxide(7.73 g, 117.3 mmol). The salt was pasteurized with agar and mortar, and allowed to react with allyl bromide(40 ml) in the presence of tributylbenzylammonium bromide(2.5 g) in dichloromethane(100 ml) for four days at the refluxing temperature of the reaction system. The product diallyl 5-allyloxyisophthalate was isolated by column chromatography(eluent; hexane : ether=10:1) . Yield 67%. Hydrolysis similar to procedure i) gave the product.

iii) 5-Hydroxyisophthalic acid(6.01 g, 32.0 mmol) and potassium hydroxide(7.17 g, 128.0 mmol) were dissolved in ethanol(50 ml) and water(30 ml), allyl bromide(2.78 g, 35.0 mmol) and potassium iodide(0.1 g) were added, and the reaction system was heated to the refluxing temperature of the system for 24 h. After 24 h, the reaction system was neutralized and cooled to room temperature. The formed solid was collected and recrystallized from water. Yield 38%.

Chemical shifts: 4.69(d with fine coupling, 2H, J=5.2 Hz, $C\underline{H}_2O$), 5.27(dd with fine coupling, 1H, J_1=10.4 Hz, J_2=1.6Hz, $\diagup C{=}C^{\diagup\underline{H}}$), 5.40(dd with fine coupling, 1H, J_1=17.2 Hz, J_2=1.6 Hz, $\diagup C{=}C_{\diagdown\underline{H}}$), 5.95~6.09(m, 1H, $CH_2C\underline{H}{=}$), 7.64(s, 2H, ), 8.06(s, 1H,



3-Allyloxyglutaric acid

To dried copper powder(1.55 g, 24.4 mmol) in a flask by gentle warming under vacuum were added diethyl 3-hydroxyglutarate(4.57 g, 23.2 mmol)(9), allyl bromide(6,48 g, 53.0 mmol) and DMF(25 ml), and allowed to react for 24 h at 65~70°C. By 24 h, all the copper usually went into solution. When the color of the solution became black, the reaction was stopped, water(100 ml) was added and the reaction system was extracted with ether(100 ml, three times). The product was isolated on column chromatography(eluent; ether: hexane=1:4). The acid was extracted from water after the hydrolysis of the product, and recrystallized from benzene. Yield 56%.

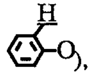
Chemical shifts: 2.65, 2.75(two dd, 4H, J_1=15.8 Hz, J_2=6.2 Hz, $C\underline{H}_2CO$), 4.09(d with fine coupling, 4H, J=5.6 Hz, $OC\underline{H}_2$), 4.23(quint, 1H, J=6.4 Hz, $OC\underline{H}$), 5.19(dd with fine coupling, 1H, J_1=10.4 Hz, J_2=1.6Hz, ${>}C=C{<}^{\underline{H}}$), 5.28(dd with fine coupling, 1H, J_1=17.2Hz, J_2=1.6 Hz, ${>}C=C_{\underline{H}}$), 5.80~6.00(m, 1H, $CH_2C\underline{H}=$), 10.4(broad s, 2H, CO_2H).

The acids(5.8 mmol) were converted into trimethylsilyl ester by the reaction with hexamethyldisilazane((1.43 g, 8.86 mmol) in the presence of ammonium sulfate(5 mg) in order to protect the carboxylic group for hydrosilylation.

Bis(trimethylsilyl) 5-allyloxyisophthalate(BSI)

b.p. 140~150°C(0.15 mmHg). Yield 83 %.

Chemical shifts: 0.38(S, 18H, $SiC\underline{H}_3$), 4.69(d with fine coupling, 2H, J=5.2 Hz, $C\underline{H}_2O$), 5.27(dd with fine coupling, 1H, J_1=10.4 Hz, J_2=1.6Hz, ${>}C=C{<}^{\underline{H}}$), 5.40(dd with fine coupling, 1H, J_1=17.2 Hz, J_2=1.6 Hz, ${>}C=C_{\underline{H}}$), 5.95~6.09(m, 1H, $CH_2C\underline{H}=$), 7.64(s, 2H,



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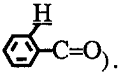


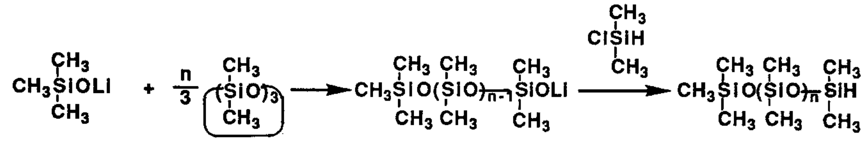
Bis(trimethylsilyl) 3-allyloxyglutarate(BSG)

b.p. 94°C(0.3 mmHg). Yield 91 %.

Chemical shifts: 0.25(s with fine coupling, 18H, $SiC\underline{H}_3$), 2.49, 2.59(two dd, 4H, J_1=15.8 Hz, J_2=6.2 Hz, $C\underline{H}_2CO$), 4.02(d with fine coupling, 4H, J=5.6 Hz, $OC\underline{H}_2$), 4.15(quint, 1H, J=6.4 Hz, $OC\underline{H}$), 5.13(dd with fine coupling, 1H, J_1=10.4 Hz, J_2=1.6Hz, ${>}C=C{<}^{\underline{H}}$), 5.22(dd with fine coupling, 1H, J_1=17.2 Hz, J_2=1.6 Hz, ${>}C=C_{\underline{H}}$), 5.75~5.95(m, 1H, $CH_2C\underline{H}=$).

Silane Terminated Oligo- and Polydimethylsiloxane

Polydimethylsiloxanes with silane(SiH) group at one end were synthesized by end-capping the living polymerization of hexamethylcyclotrisiloxane as shown in Scheme 2.

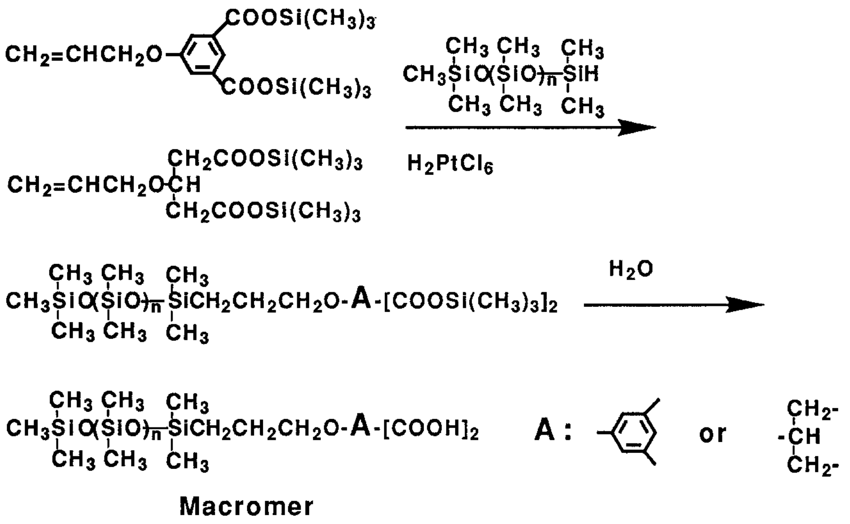


Scheme 2. Synthesis of Silane Functionalized Well-defined Polydimethylsiloxane

Pentamethyldisiloxane was synthesized by the reaction of lithium trimethylsilanolate with dimethylchlorosilane. Polydimethylsiloxane with silane function at one end of the molecule was prepared by end-capping the living anionic polymerization of hexamethylcyclotrisiloxane initiated with lithium trimethylsilanolate with excess dimethylchlorosilane(1). After the reaction, the volatile materials were removed by evacuation, and the residual prepolymer was purified by reprecipitation from THF into methanol.

Macromers

Silane terminated polydimethylsiloxane was transformed into macromer by hydrosilylation reaction as shown in Scheme 3.



Scheme 3. Synthesis of Terminal Dicarboxylic Functionalized Polysiloxane Macromer

Allyl functionalized dicarboxylic acid trimethylsilyl esters were coupled with polydimethylsiloxane by hydrosilylation reaction with silane terminated prepolymer in the presence of hexachloroplatinic acid. An example is given.

To the solution of bis(trimethylsilyl) 3-allyloxyglutarate(1.0 g, 3.0 mmol) and hexachloroplatinic acid(one drop of 0.1 mol/l solution in THF) toluene solution of the prepolymer(Mw=7000, 2.45 g, 0.35 mmol) was added at 60°C and allowed to react for 8 h. After 8 h, toluene was removed and the residual product was isolated and purified by repeated reprecipitation from THF into methanol. The terminal silyl ester function was deblocked by washing the ether solution with dilute hydrochloric acid. In case the molecular weight of the prepolymer was low(lower than 2,000), the polymer was dissolved in ether after the removal of toluene, followed by washing with dilute hydrochloric acid, and recovered by extraction.

In case of isophthalic acid functionalized macromer, the macromer was purified on column chromatography eluted first with hexane to remove unreacted prepolymer and polysiloxane formed by side reaction(see results and discussion part), followed by the elution with ether.

Number average molecular weight was estimated by titration and VPO, and molecular weight distribution was evaluated by GPC.

Results and Discussion

The results of the synthesis of silane terminated polydimethylsiloxane are shown in Table 1.

Table 1. Synthesis of Silane Terminated Polydimethylsiloxane

No.	Yield(%)	Mn,calc[a)]	Mn,VPO	Mn,Tit[b)]	Mw/Mn[c)]
1	87	10,100	7,900	7,300	1.10
2	92	8,300	7,000	8,800	1.09
3	80	5,100	4,900	4,300	1.09
4	93	4,500	4,700	5,800	1.10
5	85	3,100	2,800	3,300	1.12
6	43	2,000	2,500	2,900	1.09
7	85	1,800	1,800	1,900	1.11
8	29	1,100	1,300	1,500	1.11

a) Calculated from [M] / [I].

b) Calculated from SiH concentration determined by titrating the amount by mercury reduction method.

c) Estimated by GPC correlating to standard polystyrene.

Polymers of well-controlled molecular weight were obtained by the polymerization initiated by lithium trimethylsilanolate

The results of the synthesis of macromers are shown in Table 2 and 3.

Table 2. Characterization of Glutaric Acid Functionalized Polydimethylsiloxane Macromer

No	Feed				Macromer		
	Prepolymer		[BSG]	Yield	Mn		Mw/Mn
	Mn	mol/l	[Prepolymer]	(%)	VPO	Tit.	
2*	8,800	0.042	8.6	83	9,500	14,800	-
3	4,300	0.059	6.6	74	5,100	5,300	1.21
5	3,300	0.11	5.7	95	3,600	3,900	1.15
8	1,500	0.24	5.0	95	2,300	1,900	1.22

* Reaction at 80°C.

Table 3. Characterization of Isophthalic Acid Functionalized Polydimethylsiloxane Macromer After Purification

No	Feed				Macromer			
	Prepolymer		[BSI]	Yield	Mn			Mw/Mn
	Mn	mol/l	[Prepolymer]	(%)	VPO	Tit.	UV	
2	8,800	0.033	14.8	40	8,000	8,000	8,900	1.13
3	5,800	0.050	10.4	62	5,300	5,900	6,700	1.17
7	1,900	0.11	7.3	78	2,600	2,400	2,500	1.10

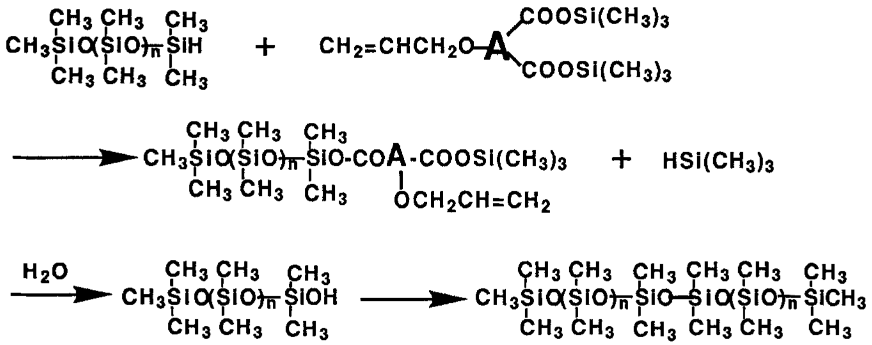
Yield of the macromer was decreased with the increase in the molecular weight of the prepolymer.

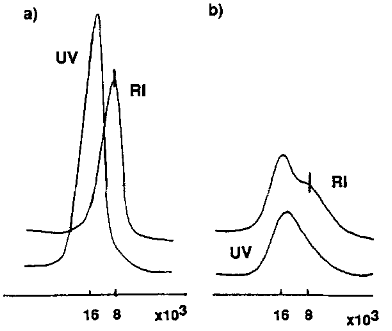
The reaction was slow at room temperature. When the reaction was carried out at 80°C(Table 2 No2), some side reaction seemed to have occurred. In GPC of the macromer after the treatment with methanol in reprecipitation procedure showed bimodal molecular weight distribution. The peak at the position which corresponds to the double in the molecular weight of the prepolymer was considerably increased. Such side reaction seems to occur even at 60°C to some extent. In experiments No. 3 and 8 of Table 2, not only the number average molecular weight determined by titration became larger than the calculated value, but also the molecular weight distribution became a little wider than that of prepolymer. However, the difference is not so large, and better-defined macromer seems to be obtained in No. 5 whose NMR were observed at 0.05 (broad s, 190H, $Si\underline{CH_3}$), 0.5(broad s, 2H, $Si\underline{CH_2}$), 1.6(broad s, 2H, $SiCH_2\underline{CH_2}$), 2.6 and 2.7(two broad s, 4H, $\underline{CH_2}CO$), 3.5(m, 2H, $\underline{CH_2}O$), 4.2(broad s, 1H, $C\underline{H}O$).

Such side reaction is more clearly indicated in the synthesis of macromer from the prepolymer which has isophthalic acid as functional group. GPC chromatograms of reaction products obtained at 60°C before and after the precipitation procedure and purified macromer are shown in Figures 1 and 2.

The unimodal peak of the reaction product became bimodal by precipitation into methanol, and the newly appeared higher molecular weight fraction does not have UV absorption as shown in Figure 1. The molecular weight of this fraction roughly corresponds to the double of that of the prepolymer in RI-detected chromatogram, while the peak position detected by UV did not change. Purification was needed to obtain macromers(see experimental part).

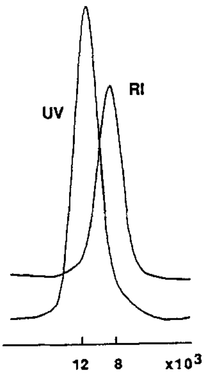
These phenomena might be explained by the ester exchange reaction during the hydrosilylation reaction.





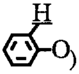
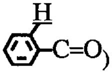
Mw corresponds to standard polystyrene

Figure 1 GPC Chromatograms of the Reaction Products a) before and b) after Precipitation Procedure into Methanol



Mw corresponds to standard polystyrene

Figure 2 GPC Chromatogram of a Purified Macromer

Although the precise reaction mechanism is not known, this assumption seems reasonable since the molecular weight of the higher molecular weight fraction is about the double of that of low molecular weight fraction. The macromer No.3 of Table 3(purified by column chromatography) whose GPC is shown in Figure 2 had the following NMR data: 0.10 (broad s, $\mathrm{SiC}\underline{\mathrm{H}}_3$), 0.6(broad s, 2H, $\mathrm{SiC}\underline{\mathrm{H}}_2$), 1.8(broad s, 2H, $\mathrm{SiCH_2C}\underline{\mathrm{H}}_2$), 4.0(m, 2H, $\mathrm{C}\underline{\mathrm{H}}_2\mathrm{O}$), 7.8(s, 2H, ), 8.4(s, 1H, ), which is consistent with the formation of well-defined macromer. The reaction conditions are very important in order to obtain well-defined macromers.

Acknowledgments

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