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Synthesis of well-defined graft copolymer with oligodimethylsiloxane and polyvinylalcohol branches

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Summary

Polyvinylalcohol macromer of well controlled molecular weight and molecular weight distribution, whose hydroxyl groups being protected as silyl ethers, was synthesized by Lewis acid catalyzed sequential silyl aldol condensation. Copolymerization of p-oligodimethylsiloxanylstyrene with the macromer, followed by the removal of the hydroxyl protective groups, gave the well-defined title graft copolymer.

Introduction

The increase in the permeability coefficient through homogeneous membrane is principally brought about by the increase in the diffusion coefficient. Accordingly the selectivity in permeation usually decreases with the increase in the permeability coefficient(1-7). In order to increase the selectivity together with the permeability coefficient, it is necessary to increase not only the diffusion coefficient but also the solubility coefficient independently and simultaneously. One possible approach to this problem is to control the density of polymer chain in micro phase-separated lamella structure of a graft copolymer as a gas permeable channel and to give selectivity in permeation by introducing functions which selectively interact with a gas molecule into this domain. Block or graft copolymers of polyvinylalcohol(PVA) and polydimethylsiloxane(PDMS) seems to be a candidate to form such micro phase-separated structure for selective oxygen permeation. Although the synthesis of such copolymers was reported starting from functionalized PDMS and vinyl acetate, the siloxane linkages were cleaved under strongly alkaline saponification condition of acetate(8-11).

Recently, Lewis acid catalyzed sequential silyl aldol condensation(Aldol Group Transfer Polymerization) of silyl enol ether with regenerated terminal aldehyde function was reported, which gives PVA having protected hydroxyl groups(12). If an aldehyde with a polymerizable double bond is used as an initiator, PVA macromer having protected hydroxyl groups as silyl ethers may be obtained. Copolymerization of p-oligodimethylsiloxanylstyrene(ODMSSt) with the macromer followed by the selective removal of the

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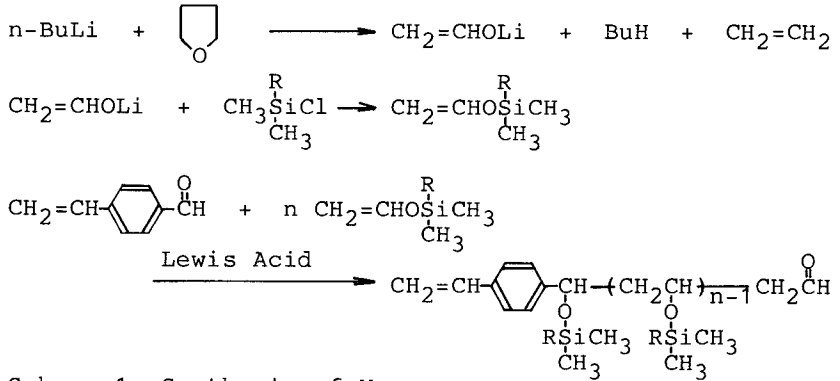
protective groups will give a well defined graft copolymer composed of PVA and oligodimethylsiloxane(ODMS).

Experimental

General

Proton NMR spectra were recorded in CCl_4 and the chemical shifts were given as δ values in ppm from tetramethylsilane as an internal standard. Molecular weight and its distribution were estimated on GPC correlating to standard polystyrene. The concentration of terminal p-vinylphenyl group in the macromer was estimated assuming the molecular distinction coefficient of the function in the polymer being same with that of model compound, 1,3-bis(t-butyldimethylsiloxy)-1-(4'-vinylphenyl)propane. Column chromatography was performed on silica gel.

Synthetic route to the macromer is shown in scheme 1.



Scheme 1. Synthesis of Macromer.

Reagents

Supplied metal salts were used after drying under vacuum(solid) or distillation(liquid).

p-Formylstyrene N, N-Dimethylformamide(DMF)(9.80 g, 0.134 mol) was reacted with p-vinylphenylmagnesium chloride prepared from p-chlorostyrene(18.4 g, 0.133 mol) and magnesium(6.50 g, 0.268 mol) in tetrahydrofuran(THF)(200 ml). The product was isolated by column chromatography using n-hexane-diethyl ether(4:1) as an eluent. The crude product was purified by distillation. 76.7% Yield. Bp 45°C(0.2 mmHg). Chemical shifts: 5.36(q, 1H, J_1=1.0 Hz, J_2=12.0 Hz, H⟩=⟨), 5.82(q, 1H, J_1=1.0 Hz, J_2=17.6 Hz, H⟩=⟨), 6.74(q, 1H, J_1=12.0 Hz, J_2=17.6 Hz, =⟨H), 7.45, 7.76(two d, 4H, J=8.2 Hz, aromatic protons), 9.92(s, 1H, CHO).

Vinyloxydimethylalkylsilane(alkyl:i-propyl, t-butyl) THF (150 ml) was reacted with n-butyllithium(1.62 N) in n-hexane(150 ml) at room temperature for 24 h. Dimethylalkyl-chlorosilane(0.222 mol) was then added drop wise at 0°C during 15 min. After further stirring for 1-2 h at the temperature all the volatile material was collected under vacuum and separated by fractional distillation.

Vinyloxydimethyl-i-propylsilane 84.9% Yield. Bp 120°C(760

mm Hg). Chemical shifts: 0.20(s, 6H, $SiCH_3$), 1.06(d, 6H, J=6.0 Hz, $CH(CH_3)_2$), 1.36(broad s, 1H, CH), 4.12(q, 1H, J_1=0.5 Hz, J_2=6.0 Hz, H\=C), 4.45(q, 1H, J_1=0.5 Hz, J_2=14.0 Hz, H\=C/), 6.45(q, 1H, J_1=6.0 Hz, J_2=14.0 Hz, =C<H).

Vinyloxy-t-butyldimethylsilane 85.8% Yield. Bp 68°C(85 mm Hg). Chemical shifts: 0.20(s, 6H, $SiCH_3$), 1.00(s, 9H, CCH_3), 4.12(q, 1H, J_1=0.5 Hz, J_2=6.0 Hz, H\=C), 4.45(q, 1H, J_1=0.5 Hz, J_2=14.0 Hz, H\=C/), 6.45(q, 1H, J_1=6.0 Hz, J_2=14.0 Hz, =C<H).

3-(t-Butyldimethylsiloxy)-3-(4'-vinylphenyl)propionaldehyde

To zinc chloride(0.51 g, 3.79 mmol) in a 50 ml round bottom flask were added p-formylstyrene(0.47 g, 3.56 mol) in methylene chloride(16 ml) and t-butyldimethylchlorosilane (0.59 g, 3.73 mmol) successively at room temperature. The desired compound was isolated directly from the reaction mixture by column chromatography using n-hexane-diethyl ether(4:1) as an eluent after removal of the solvent. 45.5% Yield. Chemical shifts: -0.11(d, 6H, J=10.0 Hz, $SiCH_3$), 0.80(s, 9H, CCH_3), 2.60(m, 2H, CH_2), 5.03(m, 1H, CH), 5.12(q, 1H, J_1=0.5 Hz, J_2=10.0 Hz, H\=C), 5.60(q, 1H, J_1=0.5 Hz, J_2=17.0 Hz, H\=C/), 6.61(q, 1H, J_1=10.0 Hz, J_2=17.0 Hz, =C<H), 7.22(s, 4H, aromatic protons), 9.65(t, 1H, J=2.0 Hz, CHO).

1,3-Bis(t-butyldimethylsiloxy)-1-(4'-vinylphenyl)propane

3-(t-Butyldimethylsiloxy)-3-(4'-vinylphenyl)propionaldehyde (1.01 g, 3.47 mmol) was reduced with sodium borohydride (0.15 g, 4.02 mmol) in ethanol(3.0 ml). The product was isolated by column chromatography using chloroform as an eluent. 52.2% Yield. This compound(0.63 g, 2.16 mmol) was silylated with t-butyldimethylchlorosilane (0.48 g, 3.19 mmol) in the presence of imidazole(0.37 g, 5.38 mmol) in DMF(3.7 ml) and isolated by column chromatography using chloroform. 92.2% Yield. Chemical shifts: -0.13(d, J=10.0 Hz, 6H, $CHOSiCH_3$), -0.05(s, 6H, CH_2OSiCH_3), 0.82, 0.83(two s, 18H, CCH_3), 1.8(m, 2H, CCH_2C), 3.53(m, 2H, OCH_2), 4.73(t, 1H, J=6.0 Hz, CH), 5.08(q, 1H, J_1=1.0 Hz, J_2=11.0 Hz, H\=C), 5.55(q, 1H, J_1=1.0 Hz, J_2=18.0 Hz, H\=C/), 6.58(q, 1H, J_1=11.0 Hz, J_2=18.0 Hz, =C<H), 7.15(s, 4H, aromatic protons). UV λ_{max}=253 nm, $\varepsilon=1.80\times10^4$.

Polymerization

Vinyloxyalkyldimethylsilane was polymerized in the presence of a Lewis acid in THF under nitrogen atmosphere at room temperature using p-formylstyrene as an initiator similar to the synthesis of 3-(t-butyldimethylsiloxy)-3-(4'-vinylphenyl)propionaldehyde. Formed macromer was isolated by pouring the reaction mixture into methanol and purified by reprecipitation, and characterized by ^{1}H-NMR, IR and GPC. The molecular distinction coefficient of the terminal p-vinylphenyl group of the macromer was assumed to be the same with that of model 1,3-bis(t-butyldimethylsiloxy)-1-(4'-vinylphenyl)propane. Macromers were copolymerized with ODMSSt using 0.1 mol% AIBN as an initiator at 60°C in THF.

Results and Discussion

Since C-C double bond in p-vinylphenyl group(styrene

type double bond) is well known to be polymerized by Lewis acid very easily in the presence of a small amount of water, it is necessary to establish the reaction conditions to obtain a macromer with one polymerizable double bond at one end. The catalytic efficiency in the synthesis of t-butyldimethylsilyl protected macromers are shown in Table 1.

Table 1. Catalytic Activity of Lewis Acid in the Synthesis of Styrene Type t-Butyldimethylsilyl Protected Polyvinylalcohol Macromer

Catalyst	Yield (%)	Mnx10^{-3} Calc.	NMR	UV	VPO	GPC	Mw x10^{-3}	Mw/Mn	f[a]
none	n.p.	2.71	-	-	-	-	-	-	-
$ZnCl_2$	36.3	2.04	3.30	3.18	2.95	3.02	3.41	1.13	0.93
	69.0	4.31	5.98	4.57	4.37	4.45	5.31	1.19	0.96
	75.5	6.47	8.67	6.53	5.27	5.46	7.06	1.29	0.81
$ZnBr_2$	40.4	3.25	2.66	1.69	1.83	2.43	3.39	1.39	1.08
$CdCl_2$	47.4	2.05	2.66	2.32	2.46	2.11	2.61	1.24	1.06
$HgCl_2$	10.7	2.84	3.77	3.88	4.96	3.10	3.50	1.13	1.28
$TiCl_4$	13.9	2.77	8.52	6.97	3.39	4.36	5.24	1.20	0.51
$SnCl_4$	15.3	2.73	1.71	2.02	6.34	6.29	7.84	1.25	3.14
$AlCl_3$	29.3	2.13	2.50	3.24	2.73	3.33	4.36	1.32	0.84
$FeCl_3$	8.5	2.79	n.d.	1.92	5.44	n.d.	n.d.	n.d.	2.83
$MgCl_2$	n.p.	2.81	-	-	-	-	-	-	-
CuBr	n.p.	2.53	-	-	-	-	-	-	-

a) f=Mn(VPO)/Mn(UV). n.p.: not polymerized, n.d.: not determined. All the macromers synthesized were solid.

When strong Lewis acids like $TiCl_4$, $SnCl_4$, $AlCl_3$, or $FeCl_3$ were used as catalyst, some side reactions seem to have occurred leading to abnormal functionality f of the product. With weak Lewis acids, or in the absence of the catalyst, polymer was not obtained. Among the catalysts tested, zinc, cadmium and mercuric chlorides gave the best results. Molecular weight could be controlled by the monomer to initiator(p-formylstyrene) ratio up to about five thousand, and the terminal functionality determined by UV analysis was almost unity. Molecular weight distribution was quite narrow. The alkyl group of alkyldimethylsilyl protective group had significant effect on the easiness of the synthesis and handling of the macromer. Trimethylsilyl protection was too weak against hydrolysis and the protective groups were lost during recovery step. Isopropyldimethylsilyl protection was not sufficient, too. The macromer was waxy and difficult to purify. The polydispersity was a little higher compared with that of t-butyl protected macromer($1.30>Mw/Mn>1.15$). Furthermore, the f value of the terminal p-vinylphenyl group was considerably lower than unity.

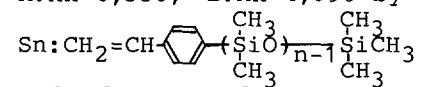
The silyl ether protection of the macromer made it possible to carry out homogeneous copolymerization reaction. The results of the copolymerization with ω-p-vinylphenyl-polydimethylsiloxane macromer are shown in Table 2.

Table 2. Copolymerization of t-Butyldimethylsilylated Polyvinylalcohol Macromer(M1)[a] with ω-p-Vinyl-

phenylpolydimethylsiloxane Macromer(M2)[b].

No.	Feed(mol%) M1	M2	Yield (%)	Composition[c] M1	M2	GPC Mw	Mn	Mw/Mn
1	3.6(A)	96.4(S2)	24.5	5.4	94.6	110	54.3	2.03
2	14.6(B)	85.4(S8)	32.2	15.3	84.7	147	37.8	3.89
3	27.8(B)	72.2(S20)	17.1	28.0	72.0	21.6	7.82	2.76

a) A:Mn=6,530, B:Mn=4,090 by UV.

b) Sn:  n=2, 8, 20

c) Mol% determined by NMR.

Macromers showed good reactivity in copolymerization to produce copolymers having almost same composition with the feed. Selective removal of t-butyldimethylsilyl protective groups from the graft copolymer in the presence of ODMS side chains was effected by heating for 10 h at 60°C in aqueous hydrochloric acid, which was shown by NMR spectrum as the disappearance of t-butyl groups and the remaining of oligodimethylsiloxanyl groups. The deprotected graft polymer behaved as hydrophilic and lyophilic gel.

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References

1. Y. Kawakami, T. Aoki, H. Hisada, Y. Yamamura and Y. Yamashita, Polym. Comm., 26, 133(1985).
2. Y. Kawakami, H. Karasawa, H. Kamiya, T. Aoki and Y. Yamashita, Polym. J., 18, 237(1986).
3. Y. Kawakami, H. Kamiya and Y. Yamashita, J. Polym. Sci.-Polym. Symp., 74, 291(1986).
4. Y. Kawakami, H. Hisada and Y. Yamashita, J. Polym. Sci.-Polym. Chem., in press.
5. Y. Kawakami, H. Kamiya and Y. Yamashita, J. Polym. Sci.-Polym. Chem. Ed., in press.
6. Y. Kawakami, T. Takikawa, T. Sugisaka and Y. Yamashita, submitted for publication in Polymer J.
7. Y. Kawakami, H. Toda, M. Higashino and Y. Yamashita, submitted for publication in Polymer J.
8. Y. Tezuka and K. Imai, Makromol. Chem. Rapid., 5, 559 (1984).
9. Y. Tezuka, A. Fukushima and K. Imai, Makromol. Chem., 186, 685(1985).
10. Y. Tezuka, S. Tanaka and K. Imai, Polym. Comm., 26, 327(1985).
11. Y. Tezuka, S. Tanaka and K. Imai, Polym. Comm., 27, 123(1986).
12. D. Y. Sogah and O. W. Webster, Macromolecules, 19, 1775(1986).

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