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Synthesis of poly(vinyl acetate) macromonomers and preparation of poly(vinyl acetate) grafted copolymers and poly(vinyl alcohol) grafted copolymers

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Poly(vinyl acetate) (PVAc) macromonomer was synthesized from the PVAc having a hydroxy group at one end prepared by a free-radical polymerization of vinyl acetate in the presence of 2-mercaptoethanol as a chain transfer agent and methacryloyl chloride. The degrees of polymerization, polydispersity index, and functionality of PVAc macromonomers were evaluated by gel permeation chromatography (g.p.c.) and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H n.m.r.). Copolymerization of the PVAc macromonomers with methyl methacrylate (MMA) and styrene (St) were carried out and traced by g.p.c., suggesting that the polymerization proceeded normally without other side reactions. The resulting polymers were confirmed to be PVAc grafted PMMA and PSt by ^{1}H n.m.r. and g.p.c. Monomer reactivity ratios between the PVAc macromonomers and the comonomers, MMA and St, were estimated from the copolymerization results. The PVAc branches in the graft copolymer were successfully led to poly(vinyl alcohol) branches by methanolysis. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(vinyl acetate); poly(vinyl alcohol); macromonomer)

INTRODUCTION

Poly(vinyl alcohol) (PVA) has been used for many industrial applications, e.g. paper-coating, fibre-sizing, as a stabilizer in disperse systems, and manufacture of fibre and film. It is often used in the blends of other polymers to improve its solution and bulk properties. Some polymers such as polyvinylpyrorridone[1,2] and cellulose and its derivatives[3] are known to be miscible with PVA in the blend films prepared by solution casting, and this seems to be caused by specific interactions, e.g. hydrogen bonding between PVA and these polymers[2]. However, many other polymer blends containing PVA are known to exhibit macroscopic phase separation. Block and graft copolymers containing the PVA sequence as one constituent have been used as compatibilizers for these blends, to attain fine dispersion, which is considered to make various properties of the blends better. These block and graft copolymers have been synthesized through various methods. The free-radical polymerization of vinyl acetate (VAc) in the presence of other polymers is often applied to the preparation of PVA blocked and grafted copolymers. However the polymers thus obtained inevitably contain homopolymers, e.g. poly(vinyl acetate) (PVAc) and added polymers, and it is generally difficult to obtain block and graft copolymers with well-defined structures from this method.

Recently, the free-radical polymerization of VAc with chain transfer agents was applied to the preparation of the block copolymers containing the PVA sequence[4]. PVA with a thiol group at one end was obtained by the polymerization of VAc in the presence of thiol acetic acid, followed by alkali catalysed methanolysis, and many kinds of block copolymers have been prepared by polymerization of various vinyl monomers in the presence of PVA[5–7]. It is expected that a molecular structure of the block copolymers will be designed by controlling polymerization conditions.

On the other hand, in order to prepare graft copolymers with a well-defined structure, one can utilize the macromonomer technique. Well-designed graft copolymers are synthesized by copolymerization of macromonomers with comonomers. Length and the content of branches in the graft copolymer can be easily analysed, then one can study the relationship between the molecular structure and the properties. There have been many reports on the synthesis of macromonomers by the various polymerization techniques, e.g. living anionic polymerization, radical polymerization by using chain transfer agents, and group-transfer polymerization. However, only a few methods of PVAc and PVA macromonomer synthesis have been developed so far[8–11], and none of these methods can be easily employed to produce a graft copolymer with PVA branches.

We reported the synthesis of the PVAc with a functional end group by free-radical polymerization using chain-transfer agents in the previous article[5] and these functional groups are considered to be useful to introduce a reactive double bond into one end of the PVAc.

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In this paper, we synthesize the PVAc macromonomer with a methacrylic double bond at one end, utilizing PVAc with a 2-hydroxyethylthio end group and methacryloyl chloride. Homopolymerization of the PVAc macromonomer and copolymerization with methyl methacrylate (MMA) and styrene (St) are carried out, and the polymerizability and the monomer reactivity ratios are estimated. The PVAc grafted copolymers are used to attempt to convert PVA grafted copolymers by methanolysis.

EXPERIMENTAL

Materials

VAc (Kuraray Company) was used without further purification. 2-Mercaptoethanol (2-ME), methanol, toluene, tetrahydrofuran (THF), *n*-hexane, and pyridine were obtained commercially with extra grade and were used without further purification. Methacryloyl chloride (MAC) of commercial grade was distilled under reduced pressure just before use. MMA and St were used after purification in the usual way. 2,2-Azobisisobutyronitrile (AIBN) recrystallized from methanol was used.

Preparation of macromonomers

The PVAc with a 2-hydroxylethylthio end group ($HOCH_2CH_2S$-PVAc) was synthesized by free-radical polymerization of VAc in the presence of 2-ME as described in the previous article[5]. The PVAc obtained was dissolved in toluene to prepare 10 wt% PVAc solution, and twice molar amount of MAC (based on hydroxy end group concentration of the PVAc) was added with stirring at room temperature in the presence of pyridine with small molar excess to MAC. After 3 h, the same molar amount of methanol was added and then excess methanol was evaporated at 30°C under reduced pressure followed by filtration of the mixture to remove the yielded salt.

The PVAc macromonomer thus obtained in toluene was used for copolymerization without further purification. A part of this solution was poured into *n*-hexane and the obtained polymer was dried under vacuum at room temperature.

Polymerization

Monomers, toluene, and AIBN were weighed into a glass flask equipped with a stirrer, a nitrogen inlet tube, and a reflux condenser. After bubbling with nitrogen, the flask was placed in a water bath at 60°C under nitrogen atmosphere. During the polymerization, a part of the polymerizing mixture was taken out of the flask at appropriate intervals to trace the copolymerization behaviour by gel permeation chromatography (g.p.c.). After the polymerization, the resulting copolymer was precipitated out of the 60/40 methanol/water mixture, which dissolves not the copolymer but the PVAc macromonomer, and was reprecipitated from an acetone solution into *n*-hexane twice.

In the case of the investigation into the monomer reactivity ratio, the polymerization was carried out as follows. Monomers, toluene, and AIBN were weighed into a glass tube, and degassed by freeze–thaw cycles, then the tube was sealed under vacuum and placed in a water bath at 60°C for a specified length of time. After the polymerization, the resulting graft copolymer was precipitated out of 60/40 methanol/water mixture and was purified as mentioned above.

Hydrolysis and acetylation

The homo- and copolymers of PVAc macromonomer were dissolved in 90/10 THF/methanol mixture followed by the addition of NaOH/methanol mixture at room temperature. After 24 h, the resulting polymer gel was neutralized by acetic acid and was washed with methanol in a Soxhlet extractor for 1 day. Acetylation of the polymers was carried out in a mixture of pyridine and acetic anhydride (1:5 by volume), at 120°C, in a test tube degassed and sealed under vacuum. After 10 h, the resulting polymer was precipitated out of *n*-hexane, and reprecipitated from an acetone solution into *n*-hexane twice.

Characterization methods

G.p.c. was taken on a Shimazu LC-6A system equipped with columns, shim-pack HSG-20H, HSG-40H, and HSG-60S, calibrated with standard polystyrenes. ^{1}H n.m.r. spectra were measured on JEOL JNM-GX500 and JNM-GSX270 spectrometers in $CDCl_3$ for PVAc macromonomers and graft copolymers having PVAc, and in DMSO-d6 for graft copolymers with PVA. ^{13}C nuclear magnetic resonance (^{13}C n.m.r.) spectra were measured on JNM-GX500 spectrometer in DMSO-d6.

RESULTS AND DISCUSSION

Synthesis and characterization of macromonomers

Figure 1 shows a ^{1}H n.m.r. spectrum of the PVAc synthesized by the free radical polymerization of VAc with 2-ME as a chain transfer agent. The peaks were assigned as shown in *Figure 1*, and the spectrum confirmed the chemical structure of $HOCH_2CH_2S$–PVAc. From the n.m.r. measurements, the number-average degree of polymerization, $\overline{Pn}$ (n.m.r.), and hydroxy group functionality of the PVAc, A_1, were calculated using following equations

$$\overline{Pn}(\text{n.m.r.}) = 2 \times (\text{area of ⑥})/(\text{area of ⑤}) + 1 \qquad (1)$$

$$A_1 = (\text{area of ④})/(\text{area of ⑤}) \qquad (2)$$

The polydispersity index, $\overline{Pw}/\overline{Pn}$, and the number-average degree of polymerization, $\overline{Pn}$ (g.p.c.) were obtained from g.p.c. measurements. *Table 1* summarizes these values. The values of $\overline{Pn}$ (n.m.r.) and $\overline{Pn}$ (g.p.c.)

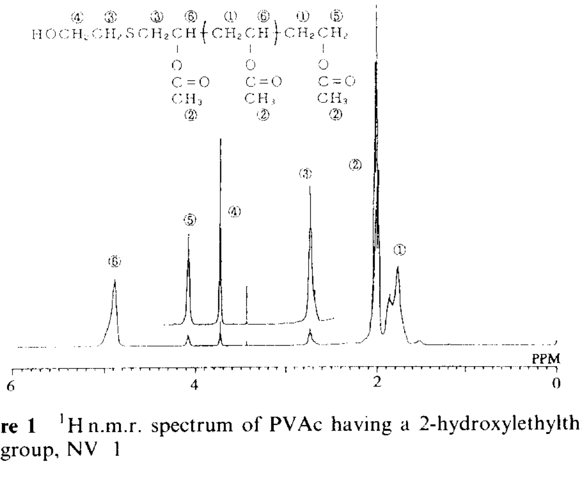

Figure 1 ^{1}H n.m.r. spectrum of PVAc having a 2-hydroxylethylthio end group, NV 1

Table 1 Characterization of PVAc macromonomers

Code	$HOCH_2CH_2S$–PVAc	$\overline{Pn}$ (n.m.r.)[a]	$\overline{Pn}$ (g.p.c.)[b]	$\overline{Pw}/\overline{Pn}$	A_1[c]	A_2[d]
NV–11–R	NV–11	20	16	1.9	0.98	0.89
NV–1–R	NV–1	31	25	2.1	0.99	0.99
NV–13–R	NV–13	57	49	2.9	0.96	0.86
NV–17–R	NV–17	107	117	3.1	0.89	0.62

[a] Number-average degree of polymerization by n.m.r.
[b] Number-average degree of polymerization by g.p.c.
[c] A_1, Functionality of a hydroxyl end group
[d] A_2, Functionality of a reactive double bond

were very close to each other for all four $HOCH_2CH_2S$–PVAc samples, having a number-average degree of polymerization from about 20 to 110. The kinetic consideration of free-radical polymerization with a chain-transfer agent predicts that under our polymerization conditions, $\overline{Pw}/\overline{Pn}$ is nearly equal to 2.0 and A_1 decreases with an increase in $\overline{Pn}$[6]. The change of A_1 with $\overline{Pn}$ was qualitatively in agreement with the theoretical prediction, and A_1 took a value near 1.0 when the degree of polymerization was very low. However, $\overline{Pw}/\overline{Pn}$ was larger than 2.0, especially when the degree of polymerization is high.

Figure 2 shows a ^{1}H n.m.r. spectrum of the PVAc macromonomer, the product (NV-1-R) of $HOCH_2CH_2S$–PVAc (NV-1) and MAC. The absorption peaks are assigned as shown in the *Figure*. It is evident by comparing the ^{1}H n.m.r. spectra in *Figure 1* and *Figure 2* that the hydroxy group of NV-1 was esterified to the methacrylate group. The PVAc having a methacrylate end group was thus successfully obtained. In *Table 1* is also listed the functionality of the PVAc macromonomers, A_2 determined by n.m.r. measurement. Since all the hydroxyl end groups were not transferred to an ester group by the reaction of $HOCH_2CH_2S$–PVAc and MAC depending on condition, A_2 was often different from A_1. *Figure 3* shows the n.m.r. spectra of $HOCH_2CH_2S$–PVAc before (*Figure 3a*) and after (*Figure 3b*) the reaction with MAC. Peak 1 shifted to peak 4 during the reaction, and peak 5 suggested the unreacted hydroxyl end group. Moreover, a new peak between peaks 3 and 4 was seen, and it was considered that this broad peak came from poly(PVAc macromonomer), and was yielded by the peak shift from peak 4. This peak shift seemed to be caused by the polymerization of PVAc macromonomer which occurred by drying the PVAc macromonomer to prepare a sample for the measurement. Therefore, we estimated A_2 by the following equation

$$A_2 = A_1 - [(\text{area of peak ⑤}) \times (1 + A_1)]/(\text{area of peaks between ④ and ⑤}) \quad (3)$$

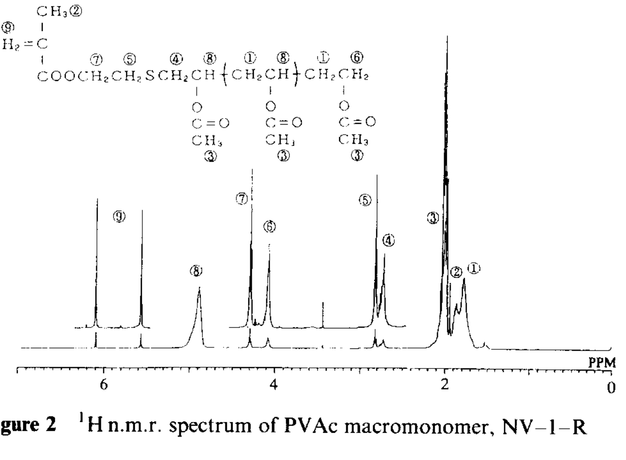

Figure 2 ^{1}H n.m.r. spectrum of PVAc macromonomer, NV–1–R

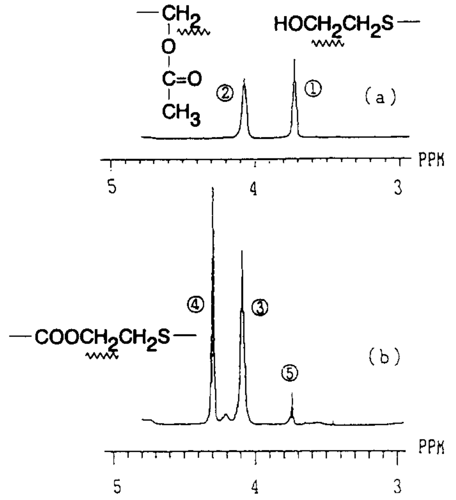

Figure 3 ^{1}H n.m.r. spectra of (a) $HOCH_2CH_2S$–PVAc, NV–11 and (b) PVAc macromonomer, NV–11–R on ester carbon

Polymerization of macromonomers

Table 2 shows the conditions and results of PVAc macromonomer polymerization. The g.p.c. traces of the polymerization are shown in *Figure 4*. With the polymerization proceeding, the peak of the PVAc macromonomer between 24 and 26 min decreased in height. On the other hand, the peak of the yielded polymer appeared between 18 and 22 min, and increased, keeping the peak positions constant. This result indicates that the polymerizations of the PVAc macromonomer proceed normally without other side reactions.

In *Tables 3* and *4* are shown the conditions and results of the copolymerization of the PVAc macromonomer with MMA and St. The g.p.c. curve of the obtained copolymer, G3-1 after precipitation, is shown in *Figure 5*. By comparing the g.p.c. charts in *Figures 4a* and *5*, it is obvious that the unpolymerized PVAc macromonomers were removed entirely by the repeated precipitation. In *Figure 6* are shown the ^{1}H n.m.r. spectra of the copolymers, indicating that copolymers of PVAc grafted PMMA and PVAc grafted PSt were successfully obtained. In *Tables 3* and *4* are shown the compositions

Table 2 Homopolymerization and copolymerization of PVAc macromonomers (M_2) with MMA and St (M_1)

Code	Monomer M_1	Monomer (g)	PVAc macromonomer	PVAc macromonomer (g)	Toluene (g)	AIBN (g)	Feed M_2 (mol%)	Time (h)	Yield (wt%)	Copolymer M_2 (mol%)
G5	MMA	50.0	NV-1-R	25.0	75.0	0.375	1.7	5.0	32.3	1.2
G6	St	25.0	NV-1-R	50.0	75.0	0.375	6.8	7.5	45.2	10.2
G13	–	–	NV-13-R	195.0	130.0	1.950	–	8.0	9.5	–

Table 3 Copolymerization of PVAc macromonomers (M_2) with MMA

Code	MMA (g)	PVAc macromonomer M_2	PVAc macromonomer (g)	Toluene (g)	AIBN (g)	Feed M_2 (mol%)	Time (h)	Yield (wt%)	Copolymer M_2 (mol%)
G14-1	10.0	NV-11-R	5.0	15.0	0.015	2.4	2.0	11.4	1.8
G14-2	9.0	NV-11-R	6.0	15.0	0.015	3.1	1.5	6.2	2.5
G14-3	7.5	NV-11-R	7.5	15.0	0.015	4.6	1.5	6.5	3.7
G14-4	5.0	NV-11-R	10.0	15.0	0.015	8.8	1.5	8.1	7.3
G3-1	10.0	NV-1-R	5.0	15.0	0.015	1.7	3.0	16.2	1.3
G3-2	7.5	NV-1-R	7.5	15.0	0.015	3.4	3.0	16.7	2.7
G3-3	5.0	NV-1-R	10.0	15.0	0.015	6.5	3.0	17.4	4.6
G3-4	2.0	NV-1-R	10.0	12.0	0.012	14.8	3.0	21.2	8.9
G13-1	10.0	NV-13-R	5.0	15.0	0.015	0.85	3.0	14.6	0.62
G13-2	7.5	NV-13-R	7.5	15.0	0.015	1.7	3.0	13.1	1.5
G13-3	5.0	NV-13-R	11.0	16.0	0.016	3.6	3.0	19.9	3.1
G13-4	8.8	NV-13-R	5.8	14.6	0.015	1.2	3.0	10.6	0.80

Table 4 Copolymerization of PVAc macromonomers (M_2) with St

Code	St (g)	PVAc macromonomer M_2	PVAc macromonomer (g)	Toluene (g)	AIBN (g)	Feed M_2 (mol%)	Time (h)	Yield (wt%)	Copolymer M_2 (mol%)
G30-1	13.0	NV-11-R	2.0	15.0	0.015	0.77	10.0	11.4	1.1
G30-2	12.0	NV-11-R	3.0	15.0	0.015	1.2	10.0	6.2	1.8
G30-3	10.0	NV-11-R	5.0	15.0	0.015	2.4	10.0	6.5	3.0
G30-4	7.5	NV-11-R	7.5	15.0	0.015	4.8	10.0	8.1	6.5
G4-1	8.0	NV-1-R	1.6	9.6	0.0096	0.72	11.8	16.2	1.1
G4-2	8.0	NV-1-R	4.0	12.0	0.012	1.8	11.8	16.7	2.6
G4-3	6.0	NV-1-R	6.0	12.0	0.012	3.5	11.8	17.4	4.3
G4-4	2.9	NV-1-R	5.8	8.7	0.0087	6.7	11.8	21.2	9.9
G31-1	13.0	NV-13-R	2.0	15.0	0.015	0.27	10.0	14.6	0.44
G31-2	12.0	NV-13-R	3.4	15.4	0.015	0.50	10.0	13.1	0.67
G31-3	10.0	NV-13-R	5.0	15.0	0.015	0.88	10.0	19.9	1.2
G31-4	7.5	NV-13-R	7.5	15.0	0.015	1.8	10.0	10.6	2.4

of the graft copolymers calculated from the n.m.r. spectra as follows.

$$(\text{mol\% of } M_2 \text{ in copolymer}) = [(\text{area of ②})/(\overline{Pn}(\text{n.m.r.}) - 1)]/[(\text{area of ⑥})/n + (\text{area of ②})/(\overline{Pn}(\text{n.m.r.}) - 1)] \times 100 \quad (4)$$

where $n = 3$ and $n = 5$ are for MMA and St respectively.

The monomer reactivity ratios between the PVAc macromonomers and the comonomers were estimated with the data in *Tables 3* and *4*. Since the conventional Mayo–Lewis copolymerization equation is approximated to equation (5) under the limit condition of $[M_1]/[M_2] \gg 1$, we can apply equation (5) to the estimation, where M_1 and M_2 are the comonomer and the PVAc macromonomer respectively.

$$(d[M_1]/d[M_2]) = r_1([M_1]/[M_2]) \quad (5)$$

The monomer reactivity ratios thus determined are shown in *Table 5*. In the case of copolymerization with MMA, the r_1 values were about 1.3, irrespective of $\overline{Pn}$ (n.m.r.), which suggests that a growing radical of MMA attacks MMA monomer more frequently than PVAc macromonomer. On the other hand, the r_1 values of the copolymerization with St were about 0.6–0.7, which means that a growing radical of St attacks the PVAc macromonomer more frequently. These results seem reasonable, because the PVAc macromonomers in this

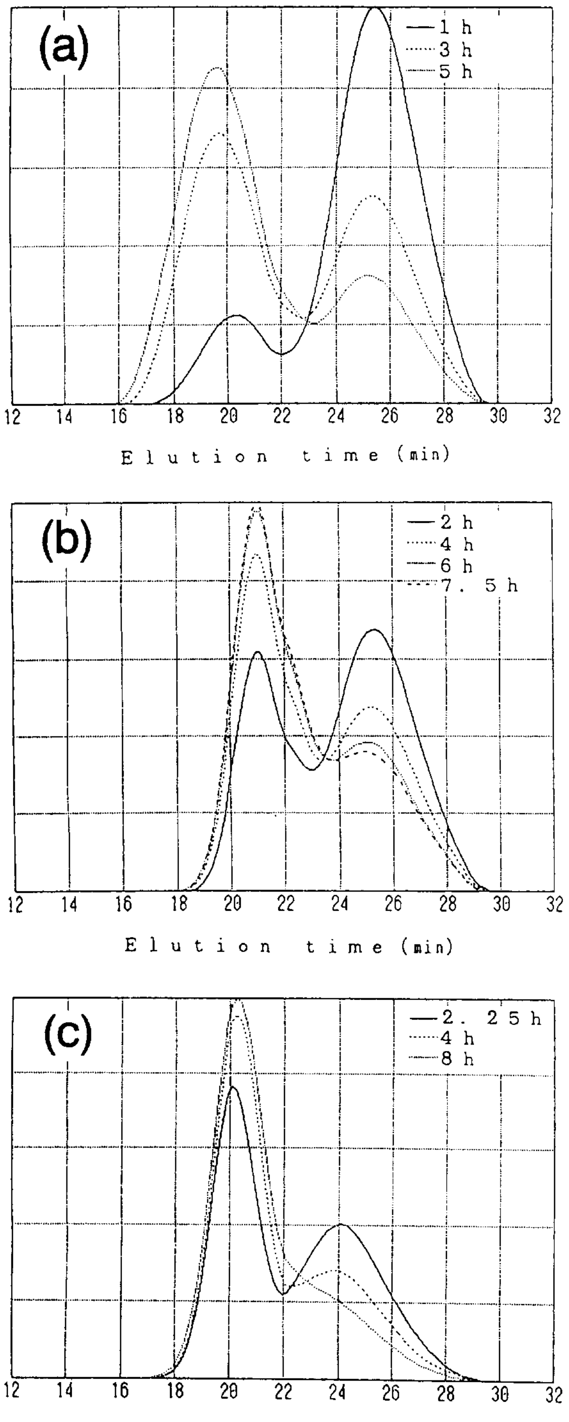

Figure 4 G.p.c. traces of copolymerization of PVAc macromonomer with (a) MMA, (b) St, and (c) homopolymerization

study have a methacrylate end group. The r_1 dependence on the degree of polymerization looks unclear. It may be due to polydispersity of the PVAc macromonomers.

PVA grafted copolymer

The PVA grafted copolymers were expected to be derived from the PVAc grafted copolymers by methanolysis. However, the PVAc grafted copolymers synthesized in this work have ester linkages, which may be cut out by methanolysis, at junction points of a mainchain and PVAc branches. Then, in order to investigate hydrolysis or transesterification of the methacrylic ester unit under the PVAc methanolysis condition, the methanolysis of poly(PVAc macromonomer) was carried out. In *Figure 7* is shown the ^{13}C n.m.r. spectrum of the product of methanolysis of poly(PVAc macromonomer). Only two kinds of ester group carbon, which are assigned to the groups in VAc and the junction point, were observed. If the cleavage occurs, C*-carbon absorptions of -C*OOCH$_3$, -C*OOH, or -C*OO$^-$ should also be observed. Therefore, it was concluded that the methacrylic ester unit of the poly(PVAc macromonomer) is hardly affected by the methanolysis

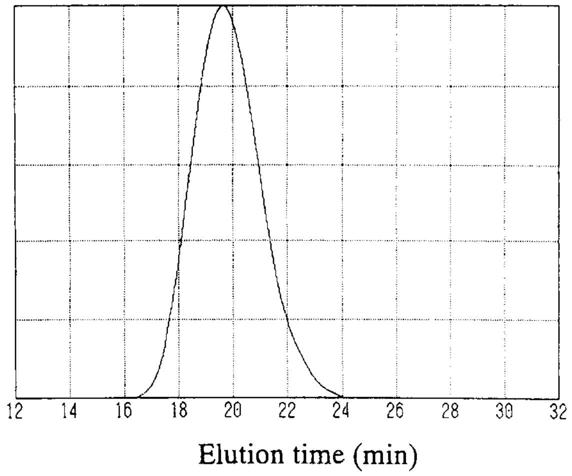

Figure 5 G.p.c. chart of PVAc grafted PMMA, G3-1 after precipitation

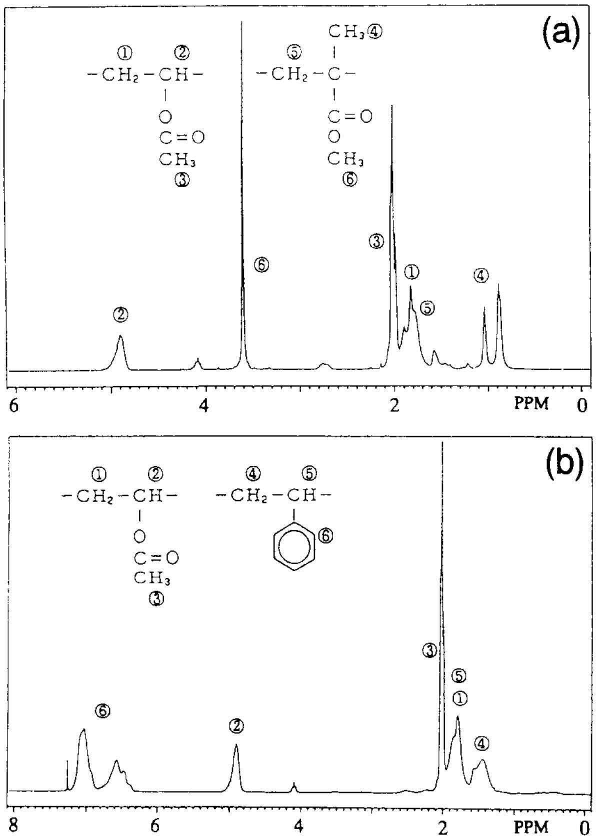

Figure 6 ^{1}H n.m.r. spectra of (a) PVAc grafted PMMA, G3-3 and (b) PVAc grafted PSt, G4-3

Table 5 Monomer reactivity ratios for copolymerization of PVAc macromonomers (M_2) with MMA and St (M_1)

	M_2		
M_1	PVAc macromonomer	$\overline{Pn}$ (n.m.r.)	r_1
MMA	NV-11-R	20	1.3 ± 0.1
MMA	NV-1-R	31	1.3 ± 0.2
MMA	NV-13-R	57	1.4 ± 0.2
St	NV-11-R	20	0.71 ± 0.07
St	NV-1-R	31	0.64 ± 0.08
St	NV-13-R	57	0.66 ± 0.07

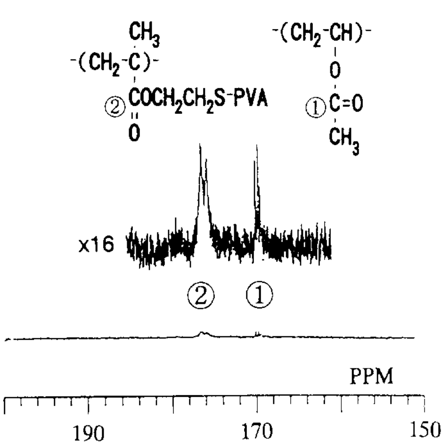

Figure 7 ^{13}C n.m.r. spectrum of product obtained by methanolysis of poly(PVAc macromonomer), G13

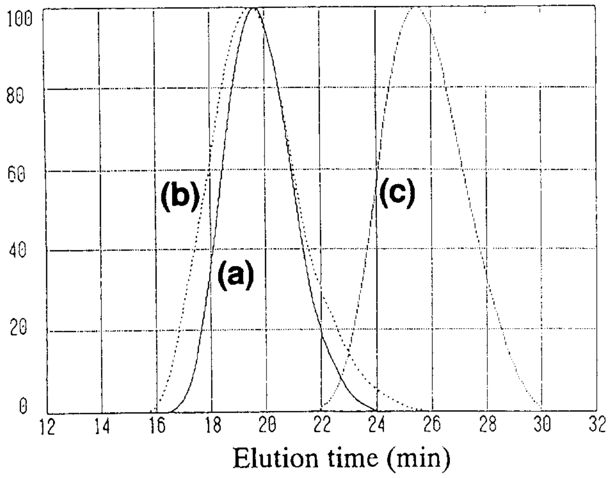

Figure 8 G.p.c. chart of PVAc grafted PMMA, G5 (a) before and (b) after methanolysis followed by acetylation, and (c) PVAc macromonomer, NV-1-R

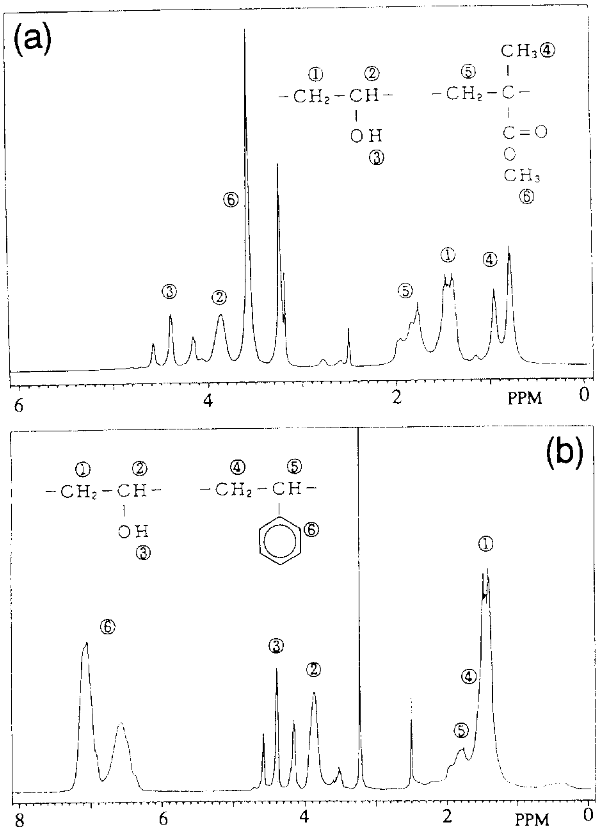

Figure 9 ^{1}H n.m.r. spectra of products obtained by methanolysis of (a) PVAc grafted PMMA, G3-3 and (b) PVAc grafted PSt, G4-3

under the conditions employed in this study. For PVAc grafted PMMA, the cleavage of the branch was checked by g.p.c. measurement. The methanolysis product of the PVAc grafted PMMA was acetylated and the resulting polymer was measured on g.p.c. *Figure 8* shows the g.p.c. chart. In *Figure 8* are also shown elution curves of the graft copolymer before methanolysis, and the macromonomer which was used for the copolymerization. The elution curves before and after methanolysis followed by acetylation were similar to each other, and no additional peak appeared after acetylation, although a new peak which corresponds to PVAc branch should appear around the macromonomer peak in *Figure 8* if the cleavage occurs. Furthermore, the content of PVAc macromonomer in the PVAc grafted PMMA was investigated by n.m.r. as described above. The contents before and after methanolysis were 1.17 mol% and 1.12 mol% respectively. As for PVAc-grafted PSt, a similar g.p.c. chart to *Figure 8* was obtained. There was no change in the elution curves before and after methanolysis followed by acetylation, and no additional peak appeared in the case of this graft copolymer. These results suggest that the cleavage of the branch does not occur and the content of the branches does not change by methanolysis. This may be partly due to the steric hindrance of α-methyl group in MMA and methacrylic group in the PVAc macromonomer units. In the case of PSt mainchain, hydrophobic atmosphere around the junction point of mainchain and branch may make it difficult for sodium hydroxide to approach there.

Some PVAc branched copolymers underwent methanolysis under the conditions employed above. ^{1}H n.m.r. spectra of the resulting PVA grafted copolymer are shown in *Figure 9*. Since the peaks were assigned to MMA, St, and vinyl alcohol units, and the peak of the methine proton in VAc was hardly observed, the graft copolymers having PVA branches were confirmed to be obtained by the methanolysis of the PVAc grafted copolymers.

CONCLUDING REMARKS

The PVAc having a 2-hydroxyethylthio end group was synthesized by the polymerization of VAc in the presence of 2-ME as a chain transfer agent. ^{1}H n.m.r. spectra confirmed their chemical structures, and the number-average degree of polymerization and the functionality of the end group were evaluated. PVAc macromonomers were synthesized by the reaction of the PVAc with methacryloyl chloride. The chemical structures were confirmed by ^{1}H n.m.r. and the functionality of a reactive double bond was estimated. Homopolymerization and copolymerization of the PVAc macromonomers with MMA and St were carried out. These polymerizations were traced using g.p.c. and were shown to proceed normally without other side reactions. The monomer reactivity ratios between the PVAc macromonomers, and MMA and St were estimated. The PVAc branches in the resulting graft copolymer were led to PVA by the methanolysis and graft copolymers having PVA branches were successfully obtained, whereas junction points of a mainchain and branches in the graft copolymer having PVA branches were successfully obtained, whereas junction points of a mainchain and branches in the graft copolymer remained as ester groups.

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