continued for 48 h. The precipitate was collected and recrystallized from benzene to give **21** as a white crystalline material (0.79 g, 100%): mp 365 °C; IR (Nujol) 1590, 1515, 1410, 1330, 1245, 1175, 1065, 1045, 1020, 1010, 945, 930, 910, 855, 805, 780, 765, 730, 695, and 675 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.61; H, 4.39; N, 7.15.

6,6′-*p*-Phenylenebis(2-amino-5-phenylpyridine-3-carboxaldehyde) (22). To a refluxing solution of 1 g (8 mmol) of **5** and 1 g (3 mmol) of **17a** in 20 mL of ethanol was added four drops of a 20% KOH solution in methanol. Reflux was continued for 12 h, and the precipitate was collected and recrystallized from chloroform to give 1.3 g (90%) of the corresponding bis(pyrido[2,3-*d*]pyrimidine). Hydrolysis of this material in 700 mL of 2 N HCl gave 1.1 g of **22**, recrystallized from *N*,*N*-dimethylformamide–acetone (mp >360 °C): IR (Nujol) 3510, 3360, 1665, 1605, 1515, 1280, 1175, 960, 845, 780, 740, and 700 cm^{-1}. Anal. Calcd for $C_{30}H_{22}N_4O_2$: C, 76.58; H, 4.71; N, 11.91. Found: C, 76.74; H, 4.62; N, 11.80.

2-Amino-5-phenyl-6-(2′-*p*-phenyl-3′,6′,7′-triphenyl-1,8-naphthyridinyl)pyridine-3-carboxaldehyde (23). To a refluxing mixture of 0.63 g (1.1 mmol) of **20** and 0.16 g (1.3 mmol) of **5** in 20 mL of ethanol and 5 mL of benzene was added five drops of a 20% KOH solution in methanol. Reflux was continued for 12 h to yield the corresponding pyrido[2,3-*d*]pyrimidine in quantitative yield. Hydrolysis of this material gave **23** in nearly quantitative yield: mp >400 °C dec; IR (Nujol) 3450, 3330, 1665, 1610, 1515, 1410, 1275, 1175, 1010, 960, 950, 855, 810, 790-785, 770, 740, and 700 cm^{-1}. Anal. Calcd for $C_{44}H_{30}N_4O$: C, 83.78; H, 4.79; N, 8.88. Found: C, 83.97; H, 4.69; N, 8.76.

3,3′-*p*-Phenylenebis(2,6,7-triphenyl-1,8-naphthyridine) (25). To a refluxing solution of 0.4 g (1.5 mmol) of **19** and 0.22 g (0.7 mmol) of **18a** in 25 mL of ethanol and 15 mL of benzene was added 15 drops of a 20% KOH solution in methanol. Reflux was continued for 48 h, and the precipitate was collected and washed with boiling benzene to give a 95% yield of **25**: mp 384–385 °C (chloroform); IR (Nujol) 1595, 1515, 1390, 1335, 1250, 1205, 1175, 1065, 1060, 1050, 1010, 970, 945, 920, 910, 845, 790, 775, 765, 735, and 695 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.64; H, 4.38; N, 7.18.

3,3′-*m*-Phenylenebis(2,6,7-triphenyl-1,8-naphthyridine) (26). To a refluxing solution of 0.56 g (2 mmol) of **19** and 0.314 g (1 mmol) of **18b** in 30 mL of ethanol was added 10 drops of a 10% KOH solution in methanol. The mixture was refluxed for 24 h, filtered, and recrystallized from benzene to give 0.45 g (60%) of **26**: mp 265 °C; IR (Nujol) 1590, 1515, 1335, 1245, 1175, 1065, 1020, 1000, 955, 945, 925, 810, 790, 770, and 695 cm^{-1}. Anal. Calcd for $C_{58}H_{38}N_4$: C, 88.52; H, 4.35; N, 7.12. Found: C, 88.56; H, 4.35; N, 7.14.

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References and Notes

(1) C. G. Overberger and J. A. Moore, *Adv. Polym. Sci.*, **7**, 125 (1970), and references cited therein.
(2) H. N. Friedlander, L. H. Peebles, Jr., J. Brandrup, and J. R. Kirby, *Macromolecules* **1**, 79 (1968), and references cited therein.
(3) E. Clar, "Polycyclic Hydrocarbons", Vol. 1, Academic Press, New York, 1964.
(4) W. Bracke, *Macromolecules*, **2**, 286 (1969); Y. Imai, E. F. Johnson, T. Katto, M. Kurihara, and J. K. Stille, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2233 (1975); J. F. Wolfe and J. K. Stille, *Macromolecules* **9**, 489 (1976); S. O. Norris and J. K. Stille, *ibid.*, **9**, 496 (1976).
(5) P. Caluwe and T. G. Majewicz, *J. Org. Chem.*, **42**, 3410 (1977).
(6) W. J. Burlant and J. L. Parsons, *J. Polym. Sci.*, **22**, 249 (1956).
(7) A. Albert and W. L. F. Armarego, *Adv. Heterocycl. Chem.*, **4**, 1 (1965).
(8) A. Albert and H. Yamamoto, *J. Chem. Soc.*, 2289 (1968).
(9) G. Evens and P. Caluwe, *J. Org. Chem.*, **40**, 1438 (1975).
(10) H. Bredereck, G. Simchen, and H. Traut, *Chem. Ber.*, **100**, 3364 (1967).
(11) H. Mukamal, F. W. Harris, and J. K. Stille, *J. Polym. Sci., Part A-1*, **5**, 2721 (1967). P. M. Hergenrother and H. H. Levine, *ibid.*, **5**, 1453 (1967).

Synthesis of Graft Copolymer by Coupling Condensation through Acetalization

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ABSTRACT: A condensation coupling through acetalization is performed between hydroxyl groups on poly(vinyl alcohol) (PVA) and an aldehyde group attached to the chain end of poly(vinyl acetate) (PVAc) to produce PVA–VAc graft copolymers. The aldehyde-terminated PVAc is prepared by polymerization of VAc with monochloroacetaldehyde or monochloroacetaldehyde diethyl acetal as the chain transfer agent. The coupling reaction of PVAc with cross-linked porous beads of PVA, followed by extraction of ungrafted PVAc, permits us to estimate the fraction of PVAc carrying the terminal aldehyde group. The observed fractions range from 0.1 to 0.5. In addition to the heterogeneous grafting onto the cross-linked beads and a membrane, PVAc is grafted onto a linear PVA in dimethyl sulfoxide, which is a common solvent for both polymers. Based on the weights of the isolated graft copolymer and the two homopolymers, the number of branches in the graft copolymer is evaluated; for instance, 18 branches of PVAc with $\bar{P}_n$ of 53 are found to be coupled to the PVA backbone with $\bar{P}_n$ of 1340.

Graft copolymers have been generally synthesized either by polymerizing a monomer from initiating sites on a backbone polymer or by linking two different polymers through polymer reactions. The latter includes deactivation of an anionic living polymer with a different polymer having polar side groups such as ester and benzyl halide and condensation reactions between functional groups attached to an end of a polymer chain and to side groups of a backbone polymer. As examples of the syntheses of graft copolymers by the condensation coupling, we can mention the condensation of hydroxyl groups in a partially acetylated poly(vinyl alcohol) (PVA) with a terminal acyl chloride group of poly(vinyl acetate) (PVAc),[1] the condensation of chlorine groups in poly(2-chlorocyanurate) ester of bisphenol A with a terminal amino group of poly(methyl methacrylate),[2] and the condensation of amino groups in partially aminoacetalized PVAc with a terminal acyl chloride group on polystyrene.[3]

The present study will describe grafting through acetalization of hydroxyl groups in PVA with an aldehyde group attached to an end of PVAc chain produced by chain

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transfer polymerizations of VAc with monochloroacetaldehyde (MCA) or monochloroacetaldehyde diethyl acetal (MCADA). The reaction scheme is represented in Figure 1. As can be seen in reactions 3 and 4, acetylation of backbone PVA of graft copolymer may give a comb-type PVAc, whereas hydrolysis of the PVAc branches in the graft copolymer under an alkaline condition may yield a comb-type PVA. The latter is possible because the acetal linkage is quite stable in alkaline media. In this paper we will study not only homogeneous grafting but also heterogeneous grafting onto cross-linked PVA gels in dimethyl sulfoxide (Me_2SO), which is a common solvent for both PVA and PVAc. Use of such insoluble polymers as the substrate for grafting makes it easy to isolate the unreacted homopolymer from the reaction product. Transformation of the resulting PVA–VAc graft copolymer into the comb-type PVAc or the comb-type PVA, together with their properties, will be investigated in the future.

Experimental Section

Polymerization of VAc. VAc was distilled after partial polymerization up to a 15% conversion, and other chemicals were purified by conventional distillation. Polymerization of VAc was initiated in vacuo with azobis(isobutyronitrile) (AIBN) at 60 °C or irradiation with γ rays of 3.2×10^4 rad·h^{-1} at 20 °C. The reason for the polymerization at the relatively low temperature was to reduce the radical transfer reaction to monomer. Concentrations of the chain transfer agents added to monomer, together with other polymerization conditions, are shown in Tables I and II. After allowing the polymerization to proceed for a given time, we recovered the VAc polymer from the polymerization mixture by precipitation with *n*-hexane followed by dissolution in acetone and precipitation in water. After boiling water extraction of the chain transfer agents occluded in the polymer, the polymer was dried at 80 °C under reduced pressure.

The polymerization results are summarized in Tables I and II for the AIBN and radiation polymerizations, respectively. Viscosity-average degrees of polymerization, $\bar{P}_v$, were calculated from $[\eta] = 7.94 \times 10^{-3}\bar{P}^{0.62}$ in acetone at 30 °C.[4] Vapor pressure osmometry on A-6 ($\bar{P}_v = 73$) revealed that the number-average degree of polymerization, $\bar{P}_n$, was 53. Chain transfer constants calculated from dependence of $\bar{P}_v$ on the chain transfer agent concentration of the monomer mixtures are 5.0×10^{-2} for MCA and 1.3×10^{-2} for MCADA at 20 °C. The constant at 60 °C for MCA is 9.8×10^{-2}. As given in Table II, the $\bar{P}_v$ of PVAc obtained by polymerization at 20 °C without the chain transfer agents was as high as 8100. The PVAc materials were subjected to grafting without fractionation, except A-2 which was obtained by fractionation of A-1.

The VAc polymer having aldehyde groups at both chain ends is a product of acetylation of PVA oxidized with sodium periodate to cleave selectively the 1,2-glycol bonds in PVA. $\bar{P}_v$ of this PVAc is 92.

Grafting. The PVA substrates employed for grafting are a noncross-linked, soluble PVA with $\bar{P}_n$ of 1340, cross-linked porous beads, and a cross-linked membrane. The beads were prepared by electron-beam irradiation with a dose of 20 Mrads on water-swollen PVA powders that are commercially available, followed by rigorous extraction of the soluble part with boiling water. The cross-linked PVA membrane was also prepared by electron-beam irradiation. The details were described elsewhere.[5]

Grafting through acetalization of the PVA substrates with PVAc carrying a terminal aldehyde group was carried out at 40–60 °C in a Me_2SO medium with the use of HCl or H_2SO_4 as catalyst. The concentration of HCl was adjusted to 0.1 N by adding a 35% concentrated aqueous solution of HCl to the reaction mixture, while that of H_2SO_4, 0.4 N, was prepared with 98% H_2SO_4. Grafting of PVAc obtained by polymerization with the use of MCADA was always carried out in the presence of 0.1 N HCl. In this case, the reaction mixture contained sufficient water for hydrolysis of the acetal end group of the PVAc to form the aldehyde. The sulfate ester eventually formed on the PVA beads in the grafting with 0.4 N H_2SO_4 was hydrolyzed by treating the grafted gel with an excess of water.

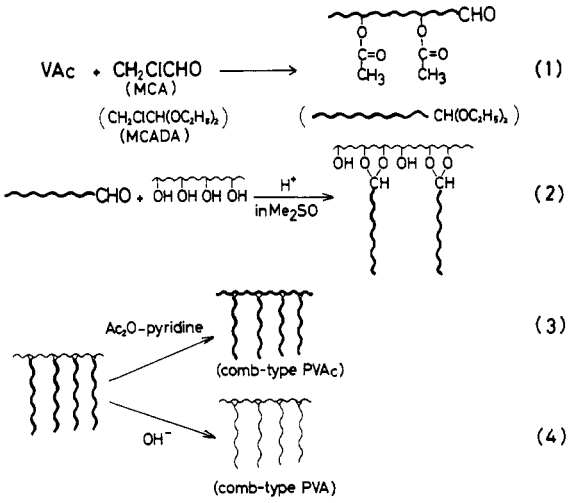


Figure 1. Reaction scheme.

Table I
Catalytic Polymerization of VAc in the Presence of Monochloroacetaldehyde Diethyl Acetal (MCADA) or Monochloroacetaldehyde (MCA) (AIBN, 60 °C)

	code no.				
	A-0	A-1	B-1	B-2	B-3
chain transfer agent (S)		MCADA	MCA	MCA	MCA
[AIBN] × 10^4, mol·L^{-1}	2.85	2.85	3.11	3.11	3.11
[S]/[VAc], by mol	0	0.325	0.085	0.133	0.180
polym time, h	6.6	12.8	22.0	29.7	36.7
conversion, %	50	9.4	4.9	3.7	4.7
$\bar{P}_v$	3030	75 (126[a])	151	65	60

[a] Fractionated, code number A-2.

Grafting onto the linear PVA proceeded throughout in homogeneous solution, while the cross-linked beads as well as the membrane remained in a swollen gel state during grafting. In all cases the reaction was allowed to proceed under agitation. Change of solution viscosity accompanying the homogeneous grafting was followed at 50 °C in an Ostwald-type viscosimeter.

Separation of Homopolymers. In the case of grafting in homogeneous solution, the reaction product was poured into 25% NaCl aqueous solution to recover the whole polymer. After the acid and NaCl were washed from the precipitates with cold water, the unreacted PVAc was extracted with ethanol and toluene. The remaining polymer was then subjected to extraction with boiling water for removal of the unreacted PVA. When the cross-linked gels were grafted, the unreacted PVAc included inside the grafted gel was extracted with Me_2SO and acetone.

Results

Change of Solution Viscosity Accompanying Grafting. Figure 2 shows the change of reduced viscosity of reaction mixtures with time. The concentration of PVA was in all cases kept to 1.0 g·dL^{-1}, and weights of added PVAc were four or eight times that of PVA. The $\bar{P}_v$ of PVAc is 73 (A-6), 124 (B-5), and 490 (A-5). It can be seen that no viscosity change occurs when only PVA or PVAc is present in the acidic solution. This fact indicates that reactions such as hydrolysis and degradation do not take place to a significant extent on both PVA and PVAc under this reaction condition (0.1 N HCl and 50 °C). It follows that the remarkable increase in solution viscosity recognized for PVA–PVAc mixtures is an indication of occurrence of grafting.

To examine whether leveling off of viscosity changes observed after about 6 h is due to attainment of an acetalization equilibrium or to other reasons such as inhibitory

Table II
Radiation Polymerization of VAc in the Presence of Monochloroacetaldehyde Diethyl Acetal (MCADA) or Monochloroacetaldehyde (MCA)[b]

	code no.						
	A-3	A-4	A-5	A-6	B-4	B-5	B-6
chain transfer agent (S)	MCADA	MCADA	MCADA	MCADA	MCA	MCA	MCA
[S]/[VAc], by mol	0	0.10	0.15	0.70	0.10	0.16	0.19
polym time, h	1.36	1.36	1.36	5.37	7.49	23.1	24.6
conversion, %	32.0	27.3	18.0	19.4	13.6	39.9	58.7
$\bar{P}_v$	8100	635	490	73[a]	201	124	103

[a] $\bar{P}_n$ = 53 (by vapor pressure osmometry). [b] 3.2 × 10^4 rad·h^{-1}, 20 °C.

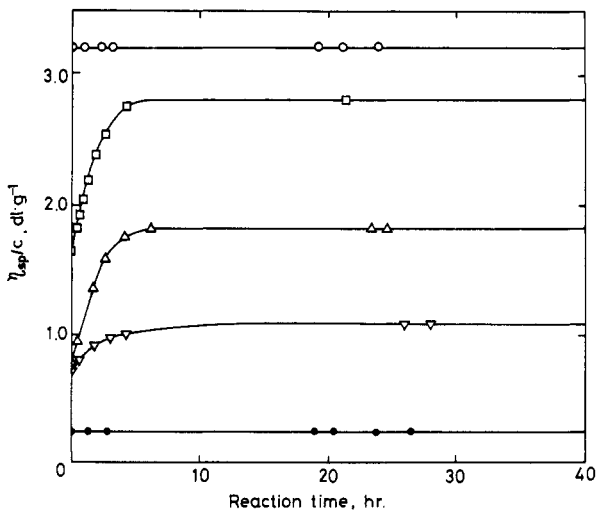


Figure 2. Variation of solution viscosity with time ([PVA] = 1.0 g·dL^{-1}, 0.1 N HCl, 50 °C): (○) PVA; (●) PVAc (B-5, [PVAc] = 4.0 g·dL^{-1}); (□) PVAc/PVA = 4 (A-5); (△) PVAc/PVA = 4 (A-6); (▽) PVAc/PVA = 8 (B-5).

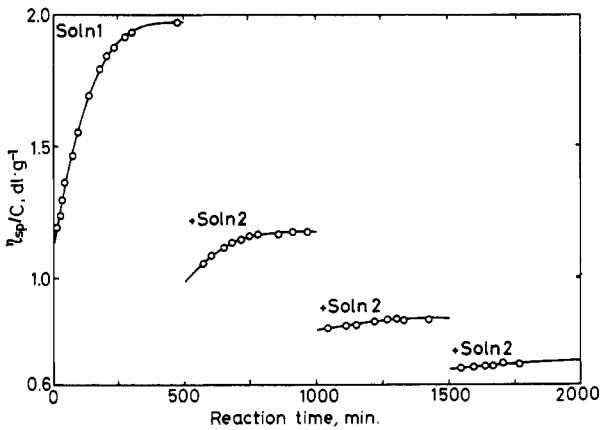


Figure 3. Variation of solution viscosity accompanying successive addition of PVAc solution (A-2, 0.1 N HCl, 50 °C): soln 1, PVAc 0.119 g, PVA 0.040 g, Me_2SO 4 mL; soln 2, PVAc 0.093 g, Me_2SO 3 mL.

effect of the grafted PVAc chains against further reactions, small amounts of PVAc prepolymer were newly added to the solution when its viscosity ceased to increase. The result is given in Figure 3. The first solution, soln 1, contains 0.119 g of PVAc (A-2) and 0.040 g of PVA in 4 mL of Me_2SO, while the added solutions, soln 2, have 0.093 g of A-2 dissolved in 3 mL of Me_2SO without PVA. As is seen in Figure 3, addition of soln 2 to soln 1 instantly brings about a large decrease in viscosity due to the dilution of solutions, followed by a gradual viscosity increase, indicating that the coupling reaction takes place further between PVA and the added PVAc. However, the extent of viscosity increase becomes very small on the third addition of soln 2. Thus one may state that 0.040 g of this PVA is capable of being grafted, at most, with 0.119 g + 3 × 0.093 g of this PVAc.

Grafting onto PVA Gels. Evidently, determination of the solution viscosity change with time gives qualitative evidence for grafting as well as a measure of the rate of coupling reaction but no information about the fraction of PVAc having the terminal aldehyde in the PVAc material used for the reaction. In this connection, grafting onto insoluble gels may provide a useful means, since the PVAc molecules without terminal aldehyde group, not being able to participate in grafting, can be separated from the reaction product with simple extraction.

To test the availability of this method, a coupling grafting onto cross-linked porous beads of PVA was undertaken with PVAc carrying aldehyde groups at both chain ends, which was obtained by oxidation of a conventional PVA with sodium periodate, followed by acetylation. Employing porous beads as the substrate for grafting is also advantageous in that these have a large specific surface area available for grafting, compared with a film, so far as grafting will be restricted to the surface region. The weight fraction of PVAc coupled to the PVA beads is given as a function of reaction time in Figure 4. The weight ratio of PVAc to PVA employed in the reaction is 0.5. As can be seen, the weight of PVAc coupled increases rapidly with time and then reaches a plateau level. In this experiment, the maximum fraction of PVAc coupled is smaller than unity, presumably because the amount of PVA gels used was not large enough to be reacted with all the reactive groups present in the added PVAc. The slight difference in the weight fraction observed between the catalysts HCl and H_2SO_4 may be explained in terms of deacetalization; the reaction mixture where HCl is the catalyst contains a small amount of water (≈0.3 mol·L^{-1}) in contrast to the mixture with H_2SO_4, and hence deacetalization seems to have taken place to some extent.

Figure 5 shows the influence of the weight ratio of PVAc to PVA on coupling of PVAc produced by the chain transfer polymerizations. It is seen that the weight of PVAc coupled increases first with increasing PVAc/PVA ratio and then reaches a plateau, although large amounts of hydroxyl groups might still remain unreacted in the beads. This suggests that grafting is confined to the surface region of the beads. Obviously, initial slopes of the curves in Figure 5 should give the weight fraction of PVAc actually having the aldehyde end group. The fractions estimated from the initial slopes are summarized in Table III. It is noteworthy that PVAc produced by the periodate oxidation has a high fraction close to unity as expected, whereas the fraction of PVAc with a terminal aldehyde (or acetal) is somewhat low for PVAc obtained by the polymerization in the presence of chain transfer agents.

Grafting was further conducted onto a cross-linked PVA membrane in Me_2SO at 30 °C for 16 h. From the results in Table IV, it is seen that the weight increase of the membrane accompanying the reaction is insignificant. Yet,

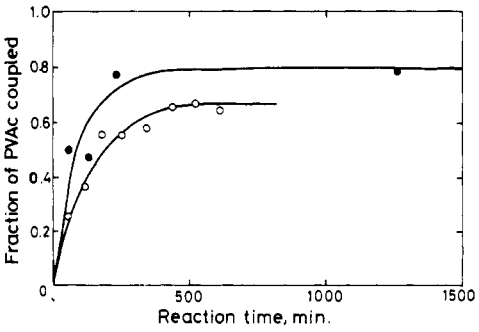


Figure 4. Reaction of PVAc obtained from IO_4^--oxidized PVA with PVA beads (PVAc/PVA = 0.5): (○) [PVAc] = 0.461 g·dL^{-1}, 0.1 N HCl, 60 °C; (●) [PVAc] = 0.487 g·dL^{-1}, 0.4 N H_2SO_4, 40 °C.

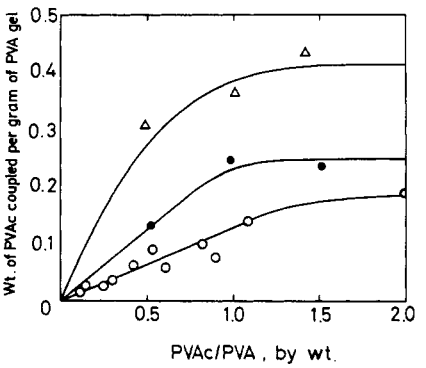


Figure 5. Influence of the PVAc/PVA ratio on grafting of PVAc onto PVA beads: (○) A-1, 0.1 N HCl, 60 °C; (●) B-1, 0.4 N H_2SO_4, 40 °C; (△) B-2, 0.4 N H_2SO_4, 40 °C.

occurrence of grafting is evident, since the contact angle against water increases as a result of grafting of PVAc which is much more hydrophobic than PVA and again decreases to the value of ungrafted membrane upon hydrolysis of the grafted PVAc.

Homogeneous Grafting onto Linear PVA. Grafting in a large scale was carried out in homogeneous solutions to obtain soluble PVA–PVAc graft copolymers. In this case, removal of homopolymers from the graft copolymer was not so easy, especially in the grafting which resulted in the formation of a graft copolymer with a relatively large number of PVAc branches. Since a selective precipitation method involves several disadvantages,[6] we adopted the conventional extraction technique in order to fractionate the product into three component polymers.

Table V gives the precipitation behavior observed when the mixtures of reaction with A-5 were poured into various solvents after being reacted for 19 h. Strong turbidity appeared on pouring the reaction products into water, irrespective of the weight ratio of PVAc to PVA, but ethanol did not cause such strong turbidity. On the other hand, the amount of polymer precipitated was much smaller when the mixture with a PVAc/PVA of 2 was poured into methanol and toluene. Interestingly, pouring the product of reaction with the PVAc/PVA ratio of 1 into methyl ethyl ketone (MEK) or acetone led to the appearance of a slight turbidity. However, when the mixture with a PVAc/PVA ratio of 2 was poured into MEK or acetone, no turbidity was observed, presumably because of micelle formation in these solvents as a result of prevention of PVA chains from association into a large particle by soluble PVAc chains.[7]

Based on the above findings, we decided to accomplish extraction of unreacted PVAc with ethanol and toluene, although it might be plausible that some of the graft copolymer would also be extracted. However, loss of a large amount of graft copolymer is not likely, since the extraction was performed for the precipitate recovered from the whole reaction mixture. The reaction products, if once precipitated, were no longer dispersed even into acetone.

From the weights of starting PVA ($W_{PVA,0}$), starting PVAc ($W_{PVAc,0}$), and unextracted PVAc (W_{PVAc}), we can calculate the percent graft, defined as ($W_{PVAc}/W_{PVA,0}$) × 100, and the grafting efficiency of PVAc, defined as ($W_{PVAc}/W_{PVAc,0}$). These are plotted against the duration of the reaction in Figures 6 and 7. The PVAc samples used are A-5 and B-5, with the PVAc/PVA ratios of 4 and 8, respectively. The reaction conditions are the same as those in the grafting shown in Figure 2. It is seen that the time dependence of the percent graft as well as the grafting efficiency is in accordance with that of solution viscosity in Figure 2, except that in the grafting with A-5 the coupling reaction still takes place, though slowly, even after a duration of 5 h.

Figures 8 and 9 illustrate the dependence of the percent graft and the grafting efficiency of PVA on the PVAc/PVA ratio, respectively. As is expected, the grafting efficiency of PVA approaches unity with an increasing PVAc/PVA ratio. In the PVAc/PVA range below 2, the percent graft appears to increase almost linearly as the PVAc/PVA becomes high, implying that the PVAc molecules having an aldehyde end group may be effectively reacted with PVA.[3]

Table III
Fraction of PVAc Having an Aldehyde End Group

	PVAc			
	A-1	B-1	B-2	IO_4^--oxidized PVAc
$\bar{P}_v$	126	151	65	92
fraction	0.13	0.25	0.54	0.96

Table IV
Grafting onto the Gel Membrane of PVA[a]

	PVAc					
	B-5			A-4		
grafted branch	none	PVAc	PVA	none	PVAc	PVA
weight increase, %		0.5	0.1		0.5	0.3
water fraction of water-swollen membrane	0.678	0.663	0.686	0.678	0.663	0.674
contact angle, deg	41.3	68.7	40.8	41.3	77.5	40.3

[a] 0.1 N HCl, 30 °C, 16 h.

Table V
Turbidity Appearing at Pouring the Reaction Mixture into Different Solvents at 25 °C[a]

	solubility		PVAc/PVA		
	PVA	PVAc	0.5	1.0	2.0
water	PS	NS	HT	HT	HT
ethanol	NS	VPS	HT	HT	MT
methanol	NS	PS	HT	MT	ST
toluene	NS	GS	HT	MT	ST
MEK	NS	GS	MT	ST	C
acetone	NS	GS	MT	ST	C

[a] Reaction: A-5, 0.1 N HCl, 50 °C, 19 h. GS, good solvent; VPS, very poor solvent; PS, poor solvent; NS, nonsolvent; HT, highly turbid; MT, moderately turbid; ST, slightly turbid; C, clear.

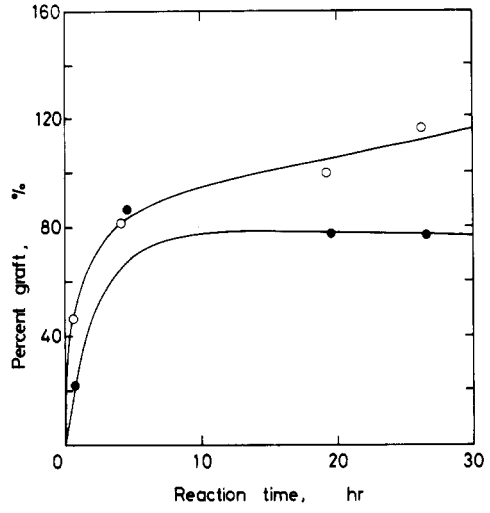


Figure 6. Dependence of percent graft on reaction time for homogeneous reaction ([PVA] = 1.0 g·dL^{-1}, 0.1 N HCl, 50 °C): (○) PVAc/PVA = 4 (A-5); (●) PVAc/PVA = 8 (B-5).

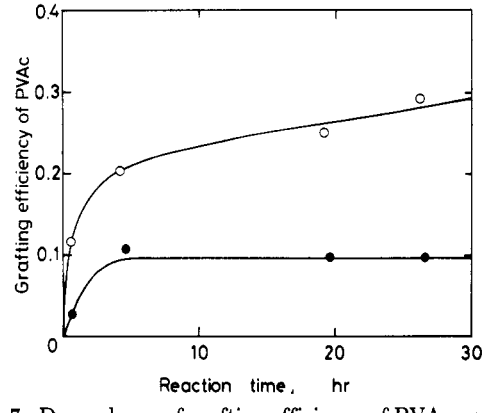


Figure 7. Dependence of grafting efficiency of PVAc on reaction time for homogeneous reaction ([PVA] = 1.0 g·dL^{-1}; 0.1 N HCl, 50 °C): (○) PVAc/PVA = 4 (A-5); (●) PVAc/PVA = 8 (B-5).

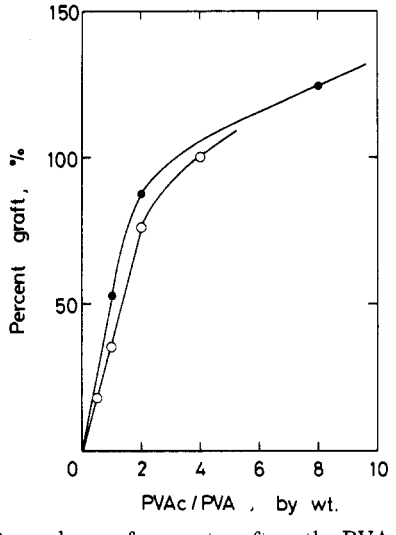


Figure 8. Dependence of percent graft on the PVAc/PVA ratio (total polymer concentration = 5.0 g·dL^{-1}, 0.1 N HCl, 50 °C): (○) A-5, 19 h; (●) A-6, 28 h.

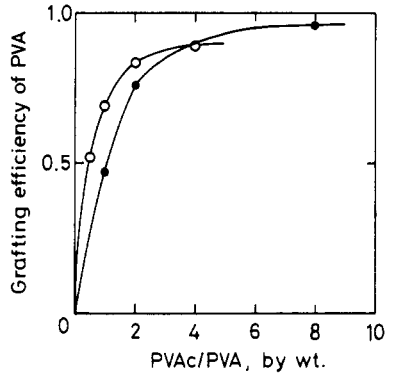


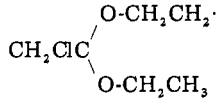
Figure 9. Dependence of grafting efficiency of PVA on the PVAc/PVA ratio (total polymer concentration = 5.0 g·dL^{-1}, 0.1 N HCl, 50 °C): (○) A-5, 19 h; (●) A-6, 28 h.

Discussion

Fraction of PVAc Having a Terminal Aldehyde Group. The synthesis of graft copolymers through condensation reactions between two different polymers requires the branch prepolymer possessing one functional end group which is reactive with some specific groups on the backbone prepolymer. Such polymers with a functional end group have often been produced by polymerizing a monomer in the presence of a chain transfer agent carrying the functional group. This method is simple but has difficulty in determining the fraction of the polymer that really carries the reactive fragment of the chain transfer agent at the chain end. Although this may be evaluated from the polymerization kinetics, the direct determination is not easy because of the extremely low content of end groups in the polymer. Recently, we have succeeded in determining the fraction by thin layer chromatography for polystyrene and poly(methyl methacrylate) polymerized using trichloroacetyl chloride and aminoethanethiol as a chain transfer agent.[8] However, this technique was not applicable for this PVAc, because attachment of only one aldehyde group to PVAc had virtually no effect on the chromatographic behavior of PVAc. A colorimetric titration has been reported to be promising for the determination of low-molecular-weight aldehydes,[9] but the molar absorption coefficient is dependent on the substituent neighboring the aldehyde group, which is not yet made clear for the PVAc used in the grafting.

In this work we attempted to utilize a grafting method with insoluble porous beads as a tool for determining the fraction of PVAc having aldehyde groups. As is demonstrated in Figure 5, this new method seems to be useful if the hydroxyl group that is accessible to the coupling reaction is available in excess and in addition the system contains no water that will bring about deacetalization of grafted PVAc chains. It may be stated that this is a kind of affinity chromatography, in which some chemical bonds as those in the coupling reactions are formed.

The observed fractions, given in Table III, are considerably smaller than unity, though addition of the chain transfer agents to monomer led to remarkable reduction in the chain length. Accordingly, it seems likely that some of the propagating radicals have abstracted hydrogen atoms directly from either aldehyde or acetal groups. For example, if the following radical is formed as a result of



a radical transfer reaction to MCADA and reinitiates the polymerization, the PVAc chain formed is not able to react with PVA, since the aldehyde resulting from hydrolysis of the acetal end group must be liberated from the polymer chain. Therefore, it may be reasonable that PVAc obtained by polymerization with MCA or MCADA has a low

content of the chain effective for acetalization with PVA.

Some Characteristics of Grafting through Acetalization. In principle, acetalization accompanies deacetalization which has, however, exceedingly low rate constants in the reaction of PVA with low-molecular-weight aldehydes. We have recently determined the rate constants of acetalization and deacetalization between PVA reactants carrying terminal aldehydes in water as well as those in Me_2SO.[10] It has been found that the deacetalization normally proceeds with an appreciable rate owing to high concentration ratios of water to aldehyde.

The influence of a small amount of water on the reaction can be seen in Figure 4, where the fraction of PVAc coupled is compared for the reactions carried out with H_2SO_4 and HCl catalysts. As the HCl concentration of the reaction mixture was adjusted to 0.1 N by addition of a 35 wt % aqueous solution of HCl, the water content of the mixture becomes 0.3 mol·L^{-1}, which is much higher than the concentration of the aldehyde group in the reaction mixtures ($\approx 10^{-3}$ mol·L^{-1}). Although the extent of deacetalization may not be remarkable at low concentrations of water, elimination of water from the reaction mixture is desired for grafting to proceed in high yields. In this connection, it should be noticed that the use of H_2SO_4 as a catalyst will accompany sulfation of PVA unless water is sufficiently present in the mixture. The resultant sulfate ester is, however, readily hydrolyzed when it comes in contact with plenty of water.

In a condensation coupling between long polymeric chains, one might expect that some steric hindrance would be operative. Slowing down of the coupling reaction observed at high extents of reaction (see Figures 6 and 8) might suggest that the condensation coupling would indeed be affected by resistance of chain interpenetration which would become more pronounced with increasing chain length.[11]

Another interesting feature of this grafting is a surface-restricted reaction observed in the grafting onto the cross-linked PVA gels. The surface reaction here does not strictly mean the reaction occurring only at the surface, but includes that occurring close to the surface.[12] Evidence of such surface grafting, found in the results in Table IV, clearly exhibits a negligibly small weight increase of membrane but an appreciable increase in water contact angle brought about by grafting. Such a reaction seems to provide a novel method for surface modification without affecting the bulk properties of the substrate polymer. According to the result in Figure 5, it appears that the porous PVA beads also prevent the PVAc molecules from free penetration into the gel. A further investigation with PVA gels of different cross-linking densities as well as with PVAc of widely different molecular weights will give valuable information on the diffusion of polymer molecules into a polymeric matrix.

Chemical Structure of Graft Copolymers. Provided that the grafted branches have the chain length identical with that of the PVAc prepolymer, the number of branches per 1000 repeating units of PVA can be calculated from the following equation with the use of the data on percent

$$\text{no. of branches} = \frac{(\text{percent graft}/100)}{\text{grafting efficiency of PVA}} \frac{1000 M_{VA}}{\bar{M}_{PVAc}}$$

grafts and grafting efficiencies of PVA, where $\bar{M}_{PVAc}$ is the molecular weight of one PVAc branch and M_{VA} is the molar weight of the repeating unit of PVA (44). The number of branches calculated from the results in Figures 8 and 9 is given in Table VI. In this calculation, M_{PVAc} is assumed to be identical with the molecular weight of the PVAc prepolymers. It is seen that the graft copolymers prepared from the PVAc with $\bar{P}_V$ of 490 possess very few branches even when the PVAc/PVA weight ratio in the reaction mixture is raised to 4. This agrees, however, well with the finding that a large portion of the PVAc has no terminal aldehyde and hence is ineffective for grafting. Since the plot of percent graft against PVAc/PVA in Figure 8 is, in nature, similar to that illustrated in Figure 5, the grafting efficiency of PVAc which is obtained from the initial slope of the curves in Figure 8 should correspond to the weight fraction of PVAc having the reactive end group. The fraction estimated from Figure 8 is 0.4 for A-5 and 0.5 for A-6. If some errors arising from the tedious isolation step of graft copolymers are taken into consideration, it appears that the agreement of these calculated fractions with those given in Table III is satisfactory. The low fraction for A-1 may be, in part, due to the high temperature (60 °C) during grafting, which would lead to significant deacetalization.

Table VI
Number of Branches of Graft Copolymers
($\bar{P}_{n,0}$ of PVA = 1340)

	PVAc A-5 ($\bar{P}_n$ of PVAc 490[a])				PVAc A-6 ($\bar{P}_n$ of PVAc 53)		
PVAc/PVA	0.5	1.0	2.0	4.0	1.0	2.0	8.0
percent graft	17.9	35.3	76.0	100.0	52.8	87.5	124.3
grafting efficiency of PVA	0.52	0.60	0.84	0.90	0.47	0.76	0.97
no. of branches[b]	0.36	0.53	0.95	1.16	10.8	11.1	12.4

[a] Viscosity average. [b] Per 1000 PVA monomer units.

As can be seen in Table VI, the graft copolymers synthesized from A-6 carry many more PVAc branches than do those from A-5. Attachment of PVAc branches to the PVA backbone may make the solubilization behavior more complicated, as demonstrated in Table V. It is interesting to point out that PVA is known to exhibit a peculiar solubility behavior when partially acetylated; for instance, the PVA acetylated by about 10 mol % is readily soluble in water without heating.

References and Notes

(1) H. W. Melville, F. W. Peaker, and R. L. Vale, *Makromol. Chem.*, **28**, 140 (1958).
(2) A. G. DeBoos and G. Allen, *Polymer*, **16**, 38 (1975).
(3) Y. Ikada, K. Maejima, and H. Iwata, *Makromol. Chem.*, **179**, 865 (1978).
(4) A. Nakajima, *Kobunshikagaku*, **6**, 451 (1949).
(5) Y. Ikada, T. Mita, F. Horii, I. Sakurada, and M. Hatada, *Radiat. Phys. Chem.*, **9**, 633 (1977).
(6) Y. Ikada, *Adv. Polym. Sci.*, **29**, 47 (1978).
(7) F. Horii, Y. Ikada, and I. Sakurada, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 323 (1974).
(8) Y. Ikada, H. Iwata, and S. Nagaoka, *Macromolecules*, **10**, 1364 (1977).
(9) E. Sawicki, T. R. Hauser, T. W. Stanley, and W. Elbert, *Anal. Chem.*, **33**, 93 (1961).
(10) H. Iwata and Y. Ikada, *Macromolecules*, **12**, 287 (1979).
(11) H. Morawetz, *J. Polym. Sci., Polym. Symp.*, **62**, 271 (1978).
(12) Y. Ikada, H. Iwata, T. Mita, and S. Nagaoka, *J. Biomed. Mater. Res.*, **13**, 607 (1979).