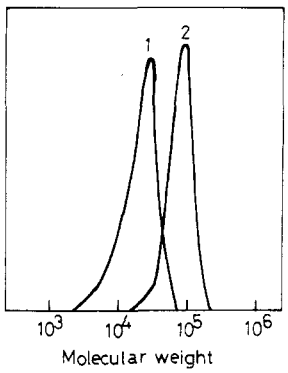

Figure 6. Molecular weight distributions of polymers obtained in runs 1 and 2 in Table IV: (1) homopolypropylene at 180 min (run 1); (2) P–R diblock copolymer at 180 + 10 min (run 2).

resulting polymers was confirmed in the ^{13}C NMR spectra.[12]

Figure 6 shows molecular weight distributions (MWD) of the resulting polymers at −70 °C. Curves 1 and 2 correspond to the MWD of polypropylene at the first stage (run 1; t = 180 min) and the MWD of the P–R diblock copolymer at the second state (run 2; t = 180 + 10 min), respectively. The MWD of the P–R diblock copolymer is clearly shifted toward higher molecular weights and remains a narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.09), indicative of the formation of a block copolymer free of homopolymer impurities. Thus, the living polymerization of α-olefin in the presence of $V(mmh)_3$–$Al(C_2H_5)_2Cl$ catalyst is also supported by the result of block copolymerization.

Registry No. $Al(C_2H_5)_2Cl$, 96-10-6; $V(mmh)_3$, 16521-95-2; polypropylene, 9003-07-0; (propene)(ethylene) (copolymer), 9010-79-1; propene, 115-07-1.

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Preparation of (*p*-Vinylbenzyl)poly(2-vinylpyridine) Macromers

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ABSTRACT: Styrene-terminated poly(2-vinylpyridine) macromers, i.e., α-(*p*-vinylbenzyl)- and α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridines), were prepared by reaction of α-lithio- and α,ω-dilithiopoly(2-vinylpyridines) with *p*-vinylbenzyl chloride, respectively. In this reaction, the α-pyridyl carbanion does not attack the vinyl group of *p*-vinylbenzyl chloride but exclusively reacts with its chloromethyl group. This selectivity leads to macromers with very high functionality (>96%) even in the case of the preparation of α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridine). A method for determining the functionality of the macromers was employed that involves copolymerization with methyl methacrylate followed by GPC analysis. The values determined by the method were confirmed by ^1H NMR spectroscopy and radical homopolymerization.

Introduction

Poly(2-vinylpyridine) (PVP) is a versatile polymer that is easily and reversibly quaternized to form quaternized water-soluble PVP that behaves as a polyelectrolyte. It is of interest with such a polymer to endow it with polymerizable group(s), i.e., to prepare PVP macromers. This macromer can be used for the preparation of well-defined types of branched polymers such as star and graft copolymers, which are expected to be useful as emulsifiers, surface modifiers, compatibilizers, etc.

Two types of PVP macromers containing *p*-isopropenylbenzyl and methacryloyl groups as polymerizable groups, respectively, were synthesized previously by Rempp et al.[1] The former type, however, is not readily subject to radical polymerization, and its numerical functionalities were not reported.

In order to equip PVP with a styrene-type functional group that is suitable for various polymerization methods, we carried out the reaction of living PVP with *p*-vinylbenzyl chloride (*p*-VBC) in the same way[2] as in the preparation of (*p*-vinylbenzyl)polystyrene macromer. It was confirmed that the carbanions of living PVP do not attack the vinyl group of *p*-VBC, facilitating the synthesis of a pure telechelic macromer. Thus, α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridine) macromer (α,ω-BVB-PVP) became possible as well. This telechelic macromer would be useful as a novel hydrophilic polymeric cross-linking reagent.

In this paper, the preparation of the PVP macromers will be described, and the results of their polymerization

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Table I
Preparation and Characterization of α-VB-PVP Macromer[a]

expt	α-lithio-PVP soln			p-VBC soln	[p-VBC]/	α-VB-PVP macromer			
	I,[b] mmol	[M]/[I]	[LE], mmol/L	[p-VBC], mmol/L	[LE]	yield, %	$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	f [d]
									0.96[e]
M-1	1.67	18.6	55.3	24.3	1.52	92	2.2	1.0_8	0.99[f]
M-2	0.358	49.7	8.7	24.3	1.46	94	5.4	1.0_5	0.99[f]
M-3	1.03	47.9	15.8	24.3	1.78	99	5.4	1.0_5	0.97[f]
M-4	0.140	225	3.5	24.3	3.08	96	24.0	1.0_8	0.98[f]

[a] Temperature of polymerization and deactivation, −78 °C; time, 30 min; solvent, THF. [b] Initiator, (1-(2-pyridyl)ethyl)lithium. [c] From GPC data. [d] Functionality, the number of vinyl groups per macromer molecule. [e] By NMR method. [f] By copolymerization method.

Table II
Preparation and Characterization of α,ω-BVB-PVP Macromer[a]

α,ω-dilithio-PVP soln			p-VBC soln	[p-VBC]/	α,ω-BVB-PVP macromer			
I,[b] mmol	[M]/[I]	[LE], mmol/L	[p-VBC], mmol/L	[LE]	yield, %	$M_n \times 10^{-3}$	M_w/M_n	f
0.450	53.3	8.0	24.3	1.34	97	1.1	1.1	1.9_3[c]

[a] Reaction conditions are the same as in Table I. Other explanatory notes are the same as in Table I. [b] Initiator, Li-naphthalene. [c] Estimated by UV method.

will be reported elsewhere in the near future.

Experimental Section

Materials. The lithio salt of 2-ethylpyridine [(1-(2-pyridyl)ethyl)lithium (2-EP-Li)] was used as initiator and was prepared and purified by recrystallization as described previously.[3] The Li-naphthalene complex was obtained by the usual method.[4] The concentrations of these carbanionic species were determined by titration (Volhard method) of bromide anion released by reaction with *n*-butyl bromide. 2-Vinylpyridine (2-VP; >98% (GC); Tokyo Kasei Kogyo Co., Ltd.) was carefully distilled under reduced pressure, was dried on a vacuum line over calcium hydride for 24 h, and was then twice distilled over a potassium mirror. *p*-VBC was synthesized according to one[5] of the known methods. It was stirred with calcium hydride for 2 days and distilled from CaH_2 on the vacuum line prior to use. THF was purified by distillation in vacuo in the presence of the sodium salt of the benzophenone dianion. Break-seal techniques were employed during all in vacuo operations.

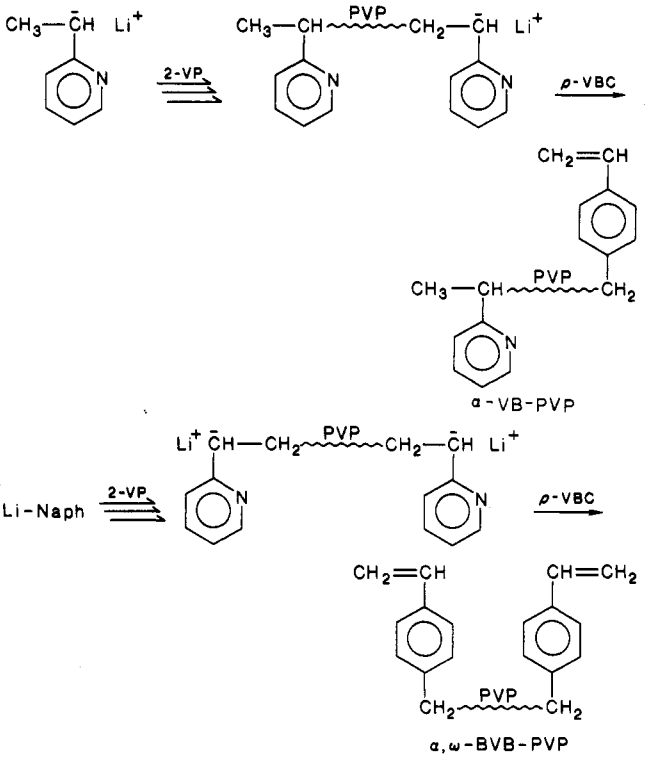
Radical Copolymerization for Determination of Macromer Functionality. For example, 80 mg of α-VB-PVP (expt M-3), 224 mg of MMA, and 1.4 mg of AIBN were charged in an ampule (ca. 5 mL), degassed by freeze–thaw cycles on a vacuum line, sealed off, and then placed in a water bath of 60 °C. After 41 h, the resulting copolymer was dissolved in ca. 2.5 mL of benzene and freeze-dried for 24 h.

Measurements. Gel permeation chromatography (GPC) was performed at a column-oven temperature of 38 °C on a Toyo Soda HLC-802UR equipped with two GMH_6 columns (61 cm × 2, Toyo Soda) or $G2000H_8$ and $G3000H_8$ columns (61 + 61 cm, Toyo, Soda). THF was used as the eluent, and the flow rate was 1.0 mL/min. The molecular weight distributions (M_w/M_n) of the polymers were calculated from their GPC curves by using a calibration curve constructed from poly(2-vinylpyridine) standards. The extent of conversion of α-VP-PVP to poly(α-VB-PVP) was determined from a GPC curve of polymer recovered after polymerization, i.e., from the area ratio of the peak of poly(α-VB-PVP) to the total response by an RI detector. ^1H NMR spectra were taken in CCl_4 at ambient temperature with a Varian XL-200 (200 MHz) FT NMR or a Hitachi R-20B (60 MHz) spectrometer. The extinction coefficients of 2-VP units and MMA units were calculated from the UV spectra, which were recorded on a Hitachi Model 200-20 spectrophotometer by using quartz cells (path length 0.2 and 1.0 cm for 2-VP and MMA units, respectively) and THF (UVS-82, Nakarai Chemicals Co. Ltd.) as solvent.

Results and Discussion

Preparation of α-VB-PVP and α,ω-BVB-PVP. In macromer synthesis, a high functionality and narrow molecular weight distribution (MWD) are of great importance. The former criterion is most important, because further purification of the macromer is usually impossible. Therefore, it is one of the objects of this study to learn how narrow MWD and high purity can be achieved in the preparation of α-VB-PVP and α,ω-BVB-PVP macromers according to Scheme I.

Scheme I



Since the propagation rate constant of anionic polymerization of 2-VP is very high, the method of adding the monomer to the reaction mixture strongly affects the MWD of PVP. In this work, 2-VP was added in the vapor phase very slowly into a solution of 2-EP-Li or Li–Naph in THF with vigorous stirring in vacuo at −78 °C. Other reaction conditions in Scheme I are listed in Tables I and II. α-VB-PVP and α,ω-BVB-PVP macromers thus obtained have a very narrow MWD, as shown in Tables I and II. Also, the gel permeation chromatograms of the macromers were sharp and symmetrical, as demonstrated in Figure 1a. For the synthesis of these macromers, if α-pyridyl carbanions react with both the chloromethyl and vinyl groups of *p*-VBC, the MWD of the macromer should

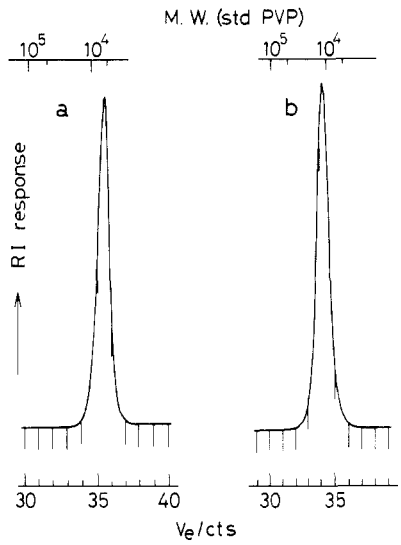


Figure 1. GPC curves of α-VB-PVP (a, expt M-2) and α,ω-BVB-PVP (b).

be broad. However, broadening of the GPC curve by chain extension of PVP is not apparent, as demonstrated in Figure 1b, and the M_w/M_n value of α,ω-BVB-PVP was as low as 1.13, even though the mole ratio of *p*-VBC to living ends ([*p*-VBC]/[LE]) was 1.34. This is in contrast to the synthesis[6] of α,ω-bis(*p*-vinylbenzyl)polystyrene macromer, which involves the reaction of two-ended polystyryllithium with *p*-VBC. This fact demonstrates that the living PVP chains do not add to the vinyl group of *p*-VBC but react only with its chloromethyl groups, confirming the fact that the rate of addition of PVP anions to styrene is extremely small.[7]

In these macromer syntheses, some advantages may be noted. Since the macromers are produced by anionic living polymerization, their molecular weights can be easily controlled. The use of 2-EP-Li as initiator results in ω-end groups of α-VB-PVP that are similar to the monomer units of PVP. Furthermore, living PVP reacts only with the chloromethyl group of *p*-VBC and does not attack the vinyl group. This has the advantages that no large excess of *p*-VBC is necessary and that no special precautions are necessary during the addition of a *p*-VBC solution to a living polymer solution, in contrast to the preparation[2] of (*p*-vinylbenzyl)polystyrene macromer.

Characterization of the Macromers. The determination of functionality of a macromer is of fundamental importance in macromer synthesis. In general, however, such a determination with a reasonable degree of accuracy is not easy, owing to the extremely small fraction of functional end groups. This difficulty may be the reason some papers concerned with macromer synthesis did not describe the numerical functionality.

In this work we employed a copolymerization method that involved radical copolymerization of α-VB-PVP with MMA[8] and the subsequent GPC analysis of the resulting copolymer as a method for determining macromer functionality. An example for α-VB-PVP will be described below.

α-VB-PVP (expt M-3) was copolymerized with methyl methacrylate by using AIBN as initiator (see Experimental Section). The resulting copolymer was subjected to GPC. Figure 2 shows the GPC curve of the copolymer by UV detector adjusted at 254 nm. It can be observed that the A and B parts of the GPC curve correspond to the uncopolymerized and copolymerized macromers, respectively, since the MMA units in the copolymer in contrast to the 2-VP units do not give a significant UV detector response;

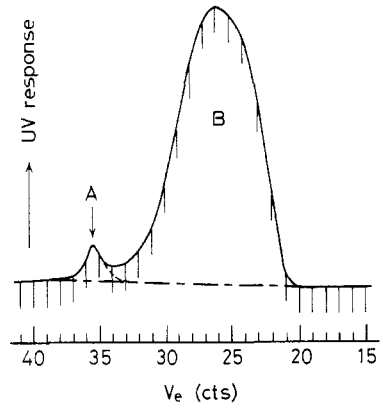


Figure 2. GPC traces of the polymer (—) obtained in the copolymerization of α-VB-PVP (expt M-3) with MMA and PMMA (- - -) as the reference: (A) uncopolymerized polymer; (B) copolymerized α-VB-PVP.

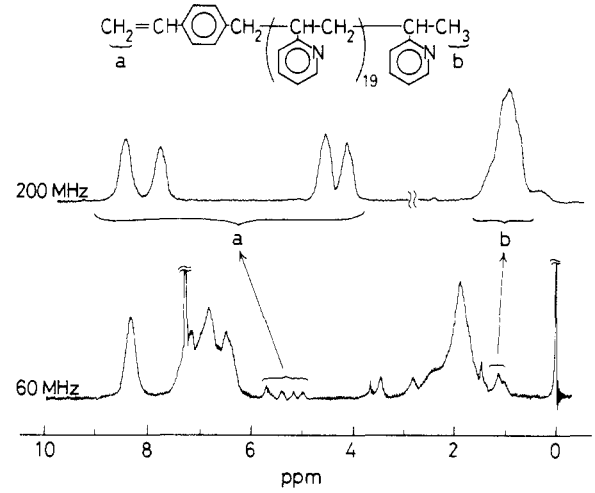


Figure 3. ^{1}H NMR spectra of α-VB-PVP (expt M-1) in CCl_4.

i.e., the extinction coefficient of 2-VP units at 254 nm in THF ($\epsilon = 2.48 \times 10^3$ L/(mol·cm)) is much larger than that of MMA ($\epsilon = 4.9$ L/(mol·cm)). The peak intensity of B is proportional to the amount of copolymerized macromer, i.e., polymer having vinyl groups. Thus, the ratio of the area of the B peak to that of total response (A + B) gives a minimum functionality, since some of peak A could be caused by macromer molecules having vinyl groups. This possibility, however, seems to be negligibly small because with very pure macromers (e.g., expt M-1 and M-2) this copolymerization method gave a functionality of 99%.

In the case of α,ω-BVB-PVP, the copolymerization method cannot be applied for the determination of the functionality, owing to gelation by the telechelic macromer. Also, a UV method using the absorption at 250 nm would not give an exact value because the pyridine rings of the macromer have a very high absorptivity of this wavelength, which was used for the determination of the vinyl groups of polystyrene macromer.[2] Thus, the wavelength of 295 nm was employed for the estimation of the functionality of α,ω-BVB-PVP, although the absorption was weak. The estimated value was 1.9_3, as shown in Table II, and this result appears to be reasonable when compared with the results in Table I.

When the molecular weight of a macromer is low, the functionality can also be determined by ^{1}H NMR. Figure 3 shows the ^{1}H NMR spectra of α-VB-PVP (expt M-1; $M_n = 2.2 \times 10^3$). The peaks of vinyl protons are clearly visible at 200 MHz. The peak intensity ratio of the vinyl protons to the methyl protons of the ω-end groups of α-VB-PVP

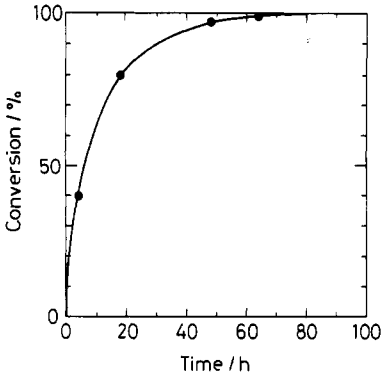


Figure 4. Time–conversion curve for the radical homopolymerization of α-VB-PVP (expt M-2). $[\alpha\text{-VB-PVP}]_0$ = 89.2 mmol/L; $[AIBN]_0$ = 16.1 mmol/L; in benzene at 60 °C.

was 1.91:3. This value is in good agreement with that obtained by the copolymerization methods, as shown in Table I.

For the alternative confirmation of the high functionality of α-VB-PVP, we carried out the radical homopolymerization of α-VB-PVP (expt M-2) under conditions of relatively high concentrations of initiator (AIBN) and macromer. Figure 4 shows the conversion of the macromer to poly(macromer) as a function of time. It is unequivocally found that α-VB-PVP is quantitatively homopolymerized to poly(α-VB-PVP), indicating the approximately 100% purity and the high polymerizability of the macromer.

Registry No. (VB)(VP)(MMA) (copolymer), 37569-87-2; poly(α-VB-PVP) (copolymer), 24980-54-9.

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(8) By this method also we obtained a reasonable value in the determination of the functionality of methacrylate-terminated polystyene macromer. In general, this method is applicable to macromers with comparatively high UV absorptivity.

Block and Graft Copolymers of Pivalolactone. 5. Graft Copolymers from Pivalolactone and Isobutylene[1]

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ABSTRACT: Isobutylene polymers have been converted to thermoplastic elastomers by the growing of pivalolactone segments at initiating sites positioned along the polyisobutylene backbone. These initiating sites were formed at benzylic carbons in poly(isobutylene-*co*-methylstyrene) by replacement of hydrogen with lithium followed by carboxylation and conversion of the carboxyls to tetrabutylammonium salts. Polymerization of pivalolactone at these sites completed the synthesis. The products could be melt-pressed to elastic films that, after orientation by drawing, had strengths up to 50 MPa. They could also be melt-spun to elastic fibers that were characterized by unusually low stress decay. This outstanding property is attributed to resistance of the polyisobutylene backbone to autoxidation.

Introduction

Block–graft copolymers of pivalolactone and isoprene studied previously possess crystalline domains formed by the polypivalolactone blocks that act as strong cross-links.[2-4] These poly(pivalolactone-*b*-isoprene-*b*-pivalolactone)-*g*-pivalolactone copolymers display stress-decay behavior similar to that observed for sulfur-cured gum rubber. Although these copolymers were protected with an antioxidant to retard autoxidation, it was suspected that the observed stress decay was due to breakdown of the polymer backbone by air autoxidation. In order to remove this vulnerability, a thermoplastic elastomeric pivalolactone copolymer system was sought that had no autoxidizable aliphatic unsaturation.

This goal was accomplished by the preparation of a graft copolymer with a polyisobutylene backbone as the rubbery phase cross-linked by means of grafted crystallizable polypivalolactone segments. The synthesis of such materials began with the copolymerization of isobutylene with a styrene, preferably a ring-methylated styrene. Lithiation of the benzylic sites in the copolymer, followed by carboxylation with carbon dioxide and conversion of the carboxyl groups to tetramethylammonium salts, afforded sites that were efficient initiators for the polymerization of pivalolactone. Poly[(isobutylene-*co*-methylstyrene)-*g*-pivalolactone] copolymers of varied composition and molecular weight have been prepared by this sequence of reactions, which is illustrated in Scheme I. This paper presents the results of a study of the preparation and characterization of these copolymers.

Experimental Section

Monomers. Isobutylene (Matheson Research Grade) was passed through two towers packed with KOH pellets and condensed into a dry ice cooled calibrated trap prior to transfer to the reaction vessel.

"Vinyltoluene" is a commercial mixture of isomers obtained from Polysciences and consists primarily of 3- and 4-methylstyrenes in a ratio of about 1:1. Styrene, α-methylstyrene, 4-methylstyrene, and α,4-dimethylstyrene were also obtained from Polysciences. All were distilled before use.

Pivalolactone was prepared as described by Blume.[5] It was passed through neutral alumina before use.

Initiators and Solvents. Alkylaluminum chlorides (Texas Alkyls) were used as received. Methyl chloride (Matheson CP Grade) was passed through two towers packed with KOH pellets prior to condensation in the reactor. Heptane (Fisher Certified Spectroanalyzed) was bubbled with dry nitrogen over 4A molecular

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