4224 *Macromolecules* 1991, *24*, 4224-4226

Effect of Pendant Functional Alcohol Residues of (*p*-Vinylphenyl)borate Copolymers on Hydrolysis

Introduction. In previous publications,[1-7] it has been shown that chemical release control, i.e., utilization of hydrolytic properties of various bonds, is an effective means of controlling release of functional compounds.

In the present paper, novel esters of an aromatic boric acid bearing a polymerizable double bond with various functional alcohols were synthesized, and the hydrolysis characteristics of their polymers and the corresponding low molecular weight compounds in an aqueous solvent were investigated for the first time in order to get basic information for the controlled release of the alcohols.

(*p*-Vinylphenyl)boric acid (**4**) was synthesized starting with *p*-bromostyrene (**1**) according to eq 1 of Scheme I. Acid **4** was esterified with various perfume and herbicide alcohols **5a–g** to afford borate ester monomers **6a–g** (eq 2, Scheme I).

Monomers **6a–g** were then copolymerized with *N*-vinyl-2-pyrrolidone (VP) to provide copolymers **6Pa–g** soluble in aqueous solvents (eq 3, Scheme II).

Copolymers **6Pa–g** in an aqueous solvent underwent hydrolysis, which released functional alcohols (**5a–g**) and left boric acid polymer **4P** behind according to eq 4 of Scheme II.

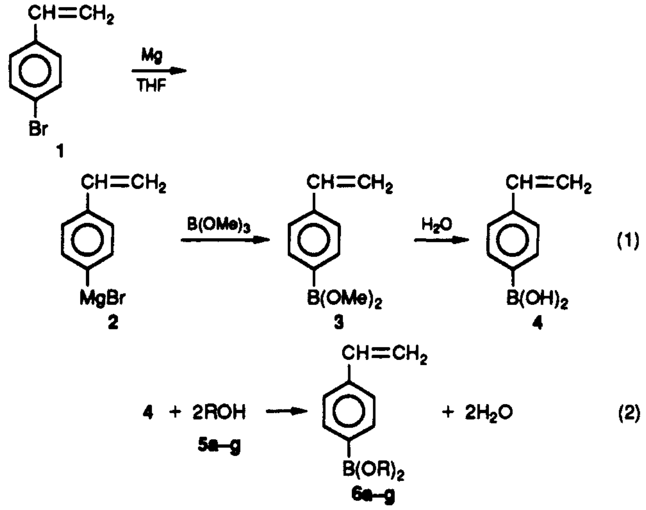
Experimental Section. (*p*-Vinylphenyl)boric Acid (4). Anhydrous THF (10 mL), dried beforehand by refluxing with $LiAlH_4$ for 24 h and stored over Na metal after distillation with exclusion of moisture, was added to the Grignard-grade magnesium (0.24 g, 10 mmol) dried by heating with exclusion of moisture under a N_2 stream. Several drops of **1** and a small piece of iodine crystal were next added, followed by heating to reflux to initiate reaction. The remaining **1** (1.9 g, 10 mmol in total) was immediately added to continue the reaction until magnesium reacted no more. Trimethyl borate (1.1 g, 10 mmol) was then added dropwise to the Grignard reagent (**2**) thus prepared with stirring at -80 °C, and stirring was continued at 20 °C for 24 h to afford **3**, which was poured into excess aqueous NaOH (5%) with vigorous stirring, followed by further vigorous stirring for 1 h. The reaction mixture was extracted with ether, and the aqueous layer was saturated with NaCl, acidified with H_3PO_4, and extracted with ether. The organic layer was worked up, and recrystallization of crude product from ether–hexane provided a white crystalline power (mp 185–187 °C) in 39% yield. Anal. Calcd for $C_8H_9BO_2$: C, 64.86; H, 6.08. Found: C, 64.92; H, 6.07. IR (KBr): 980, 900 (vinyl) cm^{-1}. NMR ($CDCl_3$): δ 3.6 (s), 5.5 (q), 6.5 (q), 7.2–7.5 (m). MS (*m/e*): 148 (M^+).

Di-β-phenethyl (*p*-Vinylphenyl)borate (6a). A solution of (*p*-vinylphenyl)boric acid (**4**; 1.5 g, 10 mmol), β-phenethyl alcohol (**5a**; 3.2 g, 20 mmol), and *p-tert*-butylcatechol (5% on the basis of **4**) in benzene (15 mL) was heated with refluxing for 24 h, with a fitted Dean–Stark trap. The reaction mixture was concentrated, and the residue was dissolved in hexane and cooled down to -70 °C to isolate an oily product, which upon vacuum drying afforded a white crystalline powder.

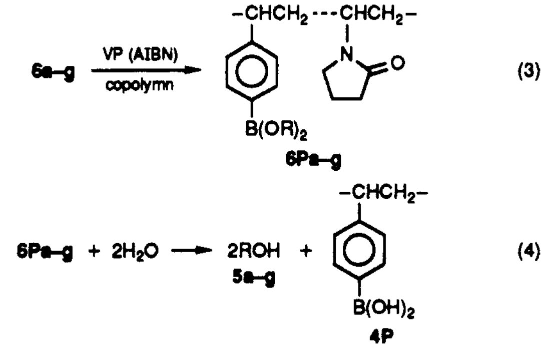
Monomers **6b–g** were synthesized in the same manner as that for **6a** to afford white crystalline powders. Table I summarizes the results thus obtained.

Copolymerization of Borate Monomers. In a typical example as given in Table II, a solution of borate monomer (**6a–g**; 20 mmol), *N*-vinyl-2-pyrrolidone (VP; 40 mmol), and α,α'-azobis(isobutyronitrile) (AIBN; 100 mg) in anhydrous dioxane (3 mL) was put into a glass ampule, which was evacuated, filled with N_2, and sealed in a conventional manner. Polymerization was carried out at 50 °C for 72 h, and the resulting polymer was precipitated into ether. IR spectra indicated a strong absorption at 1650 (C=O) cm^{-1} with disappearance of those at 1000 and 900 (vinyl) cm^{-1}.

Scheme I



Scheme II



5, 6, 6Pa, R = β-phenethyl
b, R = citronellyl
c, R = geranyl
d, R = 1-menthyl
e, R = bornyl
f, R = p-(2,4-dichlorophenoxy)ethyl
g, R = p-(2,4,5-trichlorophenoxy)ethyl

Hydrolysis of Borates. A solution of borate polymer (**6Pa–g**; 1 mmol as borate) or the corresponding model compound (1 mmol) in DMF–H_2O (5:1, v/v; 10 mL) was allowed to stand at 20 °C. The pH values of the solution lied between 6 and 7 during the standing. When 24 or 48 h had elapsed after the solubilization, the solution was extracted with ether (100 mL). The ether extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated on a rotary evaporator. The resulting residue was subjected to gas chromatography using ether as solvent, and the results were compared quantitatively with those for standard samples of alcohols (**5a–g**) to determine the amounts of the alcohols liberated by hydrolysis. The results thus obtained are given in Table III.

Results and Discussion. In order to synthesize the basic monomer **4**, **1** was converted to a Grignard reagent (**2**) with magnesium in anhydrous THF, and trimethyl borate was then added with stirring at dry ice tempera-

0024-9297/91/2224-4224$02.50/0

Table I
Boric Esters (6a–g) Prepared with Perfume and Herbicide Alcohols[a]

6a–g	R	yield, %	mp, °C	anal.[b] C, %	anal.[b] H, %	NMR,[c] ppm
6a	β-phenethyl	51	142–143	80.72 (80.90)	7.00 (7.02)	2.7 (t), 3.7 (t), 5.4 (q), 6.5 (q), 7.2 (s)
6b	citronellyl	53	126–128	78.98 (79.25)	10.49 (10.61)	0.2–2.5 (m), 3.7 (t), 5.1 (t), 5.4 (q), 6.4 (q), 7.0–7.5 (t)
6c	geranyl	49	131–132	80.12 (80.00)	9.50 (9.76)	0.5–2.4 (m), 4.1 (t), 4.5–5.7 (m), 5.5 (q), 6.5 (q), 7.0–7.5 (m)
6d	1-menthyl	40	120–121	79.20 (79.25)	10.42 (10.61)	0.5–2.6 (m), 3.5 (b), 5.5 (q), 6.7 (q), 7.2–8.0 (m)
6e	bornyl	46	116–118	80.06 (80.00)	9.76 (9.76)	0.2–2.7 (m), 4.0 (m), 5.5 (q), 6.5 (q), 7.0–7.5 (m)
6f	β-(2,4-dichlorophenoxy)ethyl	54	101–102	54.55 (54.75)	4.01 (3.99)	4.1 (b), 5.4 (q), 6.3 (q), 6.8–7.6 (m)
6g	β-(2,4,5-trichlorophenoxy)ethyl	47	110–111	48.63 (48.40)	3.09 (3.19)	4.1 (m), 5.4 (q), 6.5 (q), 6.9–8.0 (m)

[a] All values for molecular ion peak (M^+) in mass coincide with the respective molecular weights. IR (KBr) indicates vinyl absorptions around 980 and 900 cm^{-1}. [b] Values in parentheses indicate calculated values. [c] $CDCl_3$.

Table II
Copolymerization of Boric Esters 6a–g with *N*-Vinyl-2-pyrrolidone (VP)[a]

boric ester	polymer convn, %	polymer 6a–g portion,[b] mol %	polymer [η],[c] dL g^{-1}
6a	61	35.2	0.12
6b	79	34.8	0.32
6c	70	36.4	0.18
6d	60	37.2	0.17
6e	73	34.3	0.27
6f	82	33.8	0.31
6g	84	33.5	0.18

[a] For details see the Experimental Section. [b] Determined by elemental analyses. [c] In DMF at 25 °C.

Table III
Hydrolytic Behaviors of Copolymer 6Pa–g As Compared with Those of the Corresponding Boric Ester[a]

copolymer and model ester	hydrolysis ratio,[b] mol % 24 h at 20 °C	hydrolysis ratio,[b] mol % 48 h at 20 °C
6Pa	40	65
β-phenethyl phenylborate	100	100
6Pb	41	43
dicitronellyl phenylborate	100	100
6Pc	68	70
digeranyl phenylborate	100	100
6Pd	36	41
di-1-menthyl phenylborate	4	28
6Pe	58	62
dibornyl phenylborate	11	27
6Pf	52	70
bis[β-(2,4-dichlorophenoxy)-ethyl] phenylborate	82	84
6Pg	78	81
bis[β-(2,4,5-trichlorophenoxy)-ethyl] phenylborate	86	89

[a] For details see the Experimental Section. [b] The amount of **5a–g** liberated divided by the amount of the borate portion in **6Pa–g** in mole percent.

tures, followed by further stirring at room temperature (20 °C) for 24 h to afford **3**. Subsequent hydrolysis provided **4** in a reasonable yield (eq 1). The boric acid **4** was then esterified with perfume and herbicide alcohols (**5a–g**) by refluxing in benzene, with a fitted Dean–Stark trap (eq 2). The purity and yield of the resulting esters (**6a–g**) were reasonable, as judged from the results of Table I, in which primary alcohols such as β-phenethyl alcohol afforded rather higher yields than secondary ones such as 1-menthol do, presumably due to steric reasons.

Monomers **6a–g** and VP (1:2, mol/mol) provided copolymers (**6Pa–g**) soluble in aqueous solvents (eq 3). It is known from Table II that copolymerization proceeded almost satisfactorily.

Copolymers **6a–g** were then subjected to the hydrolytic study in a homogeneous medium: DMF–water (5:1, v/v), in order to get basic information on this kind of hydrolysis with reproducible results (eq 4).

Since the hydrolysis should release original alcohol (**5a–g**) and leave the hydrolysis product (**4P**) of **6Pa–g** behind (eq 4), the gas chromatographic investigations were carried out on the ether extracts of hydrolysis mixtures.

It is noted in Table III that, in the cases of **6Pd** and **6Pe** bearing secondary alcohol residues such as 1-menthyl and bornyl groups, the values of the hydrolysis ratio at 20 °C were significantly larger than those for the corresponding low molecular weight borates, whereas this relationship was just reversed for other copolymers bearing primary alcohol residues.

Since significant changes in the copolymer composition are not found and the values of intrinsic viscosity, [η], are not too small (Table II), this behavior appears to be attributable to the difference in the affinity to the aqueous solution between **6Pa–g** and the corresponding borates. Thus, the VP portion in the copolymer allows us to solubilize functional borate polymers in aqueous solvents and may affect the rate of hydrolysis, although with a dependence upon the distribution of the sequence of the borate portion in the copolymer molecule. This solubilization effect may be a cause of larger values of the hydrolysis ratio for copolymers bearing the secondary alcohol residue as compared with those for the low molecular weight models and vice versa for copolymers bearing the primary one, since the borates of the secondary alcohol employed as a model in the present study were less soluble in aqueous solvents, i.e., less hydrophilic, than those of the primary alcohol.

It can be said generally that hydrolysis of polymeric functional borate is a fast process even at room temperature, which depends on various factors, including the chemical structure and the physical state, and may be applicable to the chemical release control of functional alcohols.

Besides the features mentioned above, borate polymers of the present study permit easy separation of the functional alcohols released by hydrolysis from the remaining polymers simply by extraction, which the corresponding model borates do not.

References and Notes

(1) Paul, D. R.; Harris, F. W. *Controlled Release Polymeric Formulations*; American Chemical Society: Washington, DC, 1976.

(2) Kamogawa, H.; Okabe, S.; Nanasawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1917.

(3) Kamogawa, H.; Haramoto, Y.; Nanasawa, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 846.

(4) Kamogawa, H.; Haramoto, Y.; Nakazawa, T.; Sugiura, H.; Nanasawa, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1577.

(5) Kamogawa, H.; Mukai, H.; Nakajima, Y.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3121.

(6) Kamogawa, H.; Haramoto, Y.; Misaka, Y.; Asada, Y.; Ohno, Y.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *23*, 1517.

(7) Kamogawa, H.; Khono, H.; Kitagawa, R. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 487.

Hiroyoshi Kamogawa* and Seiyu Shiraki

Department of Applied Chemistry
Yamanashi University
Takeda 4, Kofu 400, Japan

Received November 27, 1990
Revised Manuscript Received April 29, 1991