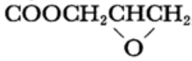
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 186—191 (1968)

Reactive Monomers Derived from *p*-Vinylbenzoic Acid

Yoshio IWAKURA,* Keikichi UNO,* Nobuo NAKABAYASHI** and Takakazu KOJIMA*

**Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo*
***Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Chiyoda-ku, Tokyo*

(Received July 5, 1967)

Reactive monomers derived from *p*-vinylbenzoic acid have been prepared which have both a vinyl group and another functional group for addition reaction or condensation reaction. The radical polymerization of these monomers gives high polymers. Monomer reactivity ratios in relation to styrene were obtained for three of these monomers. Plots of Alfrey-Price's *e* value *vs.* Hammett's σ value show a linear relationship in the case of substituted styrenes. σ values are then estimated by this relation, using *e* values based on the monomer reactivity ratios. The σ constants assumed for the COCl,  $\mathrm{COOCH_2\underset{\diagdown O \diagup}{CHCH_2}}$, and NCO substituents are 0.71, 0.64, and 0.27 respectively. These σ values are confirmed by other supporting facts.

Wide investigations of reactive polymers have been carried out in our laboratory.[1-3] Generally speaking, there are two ways to introduce reactive functional groups into macromolecules. One way is the reaction of a polymer with some compound which has functional groups. The other is the polymerization of vinyl monomers which have functional groups for a polymer reaction. Such a vinyl monomer has been called a reactive monomer.[4] The latter way is rather more favorable than the former because of the uniform composition of the polymer obtained.

The present paper will describe the preparation of reactive monomers derived from *p*-vinylbenzoic acid. The reactive groups introduced are those for addition reaction or condensation reaction: epoxide, aziridine, isocyanate, acid chloride, and

---

1) Y. Iwakura, T. Kurosaki and N. Nakabayashi, *Makromol. Chem.*, **44/46**, 570 (1961).

2) N. Nakabayashi and Y. Iwakura, *ibid.*, **81**, 180 (1965).

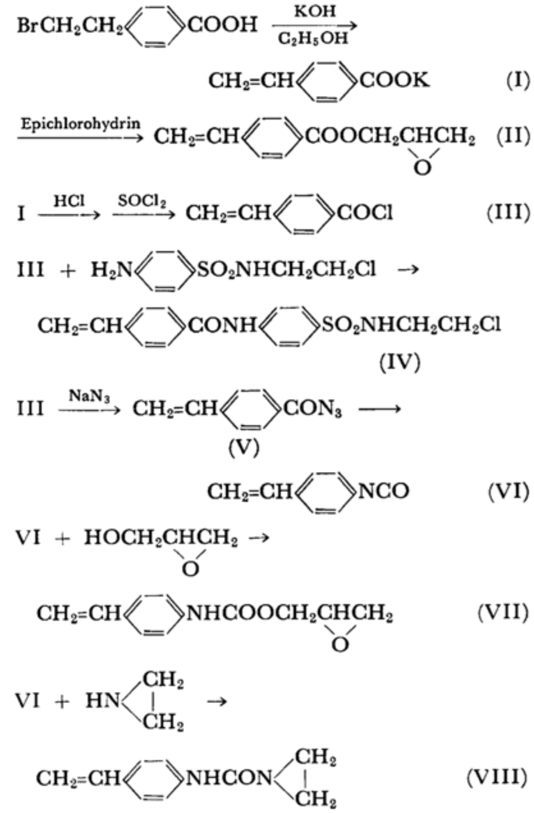
3) Y. Iwakura, T. Kurosaki, N. Ariga and T. Ito, *ibid.*, **97**, 128 (1966).

4) Y. Iwakura, K. Uno, N. Nakabayashi and T. Kojima, This Bulletin, **38**, 1223 (1965).

β-chloroethylsulfonamide. All of these monomers belong to *p*-substituted styrenes. The monomer reactivity ratios of these monomers in relation to styrene showed some correlation with the polar effect of the group.

Results and Discussion

Preparation of *p*-Substituted Styrenes. In the present study, *p*-substituted styrenes (II—VIII) were synthesized from *p*-vinylbenzoic acid[5-7] according to the following equations:



Potassium *p*-vinylbenzoate (I) was obtained according to Jäger's method. The glycidyl ester (II) was obtained in a good yield by the reaction of compound I with an excess amount of epichlorohydrin in the presence of quaternary ammonium salts serving as catalysts.

p-Vinylbenzoyl chloride (III) was prepared by Adrova.[8] In this reaction, the amount of thionyl chloride used must be carefully measured. Using an excess amount of thionyl chloride gives *p*-(α-chlorovinyl)benzoyl chloride, accompanied by a resinous polymer. The reaction of compound III with *N*-β-chloroethyl sulfanilamide[2] and sodium azide gave compound IV and compound V respectively.

A mixture of *o*- and *p*-isomers of vinylphenyl isocyanate is known to have been synthesized from *o*- and *p*-vinylaniline by phosgenation.[9] In the present study, *p*-vinylphenyl isocyanate (VI) was obtained by the Curtius rearrangement of the acid azide V. Furthermore, glycidyl urethane (VII) and *N*, *N*-ethylene urea (VIII) were derived through the reaction of VI with glycidol and aziridine respectively. The physical and infrared absorption data of these monomers are summarized in Table 1.

Polymerization of *p*-Substituted Styrenes. The radical polymerization of these monomers was carried out in a solution, using azo-bis-isobutyronitrile (AIBN) as an initiator. All of the monomers gave white powders soluble in such organic solvents as dioxane and dimethylformamide (DMF). The infrared spectra of these polymers give absorptions characteristic of the functional groups. The polymers from III and VI were very sensitive to moisture, and they became insoluble in an instant. The results of the homopolymerization of these reactive monomers are summarized in Table 2.

The isocyanates are known to undergo anionic polymerization easily even when sodium cyanide is used as an initiator.[10] On the other hand, styrene does not give any polymer in the presence of sodium cyanide. The compound VI has both vinyl and isocyanate groups; an anionic polymerization of it in DMF with sodium cyanide as an initiator was undertaken. The polymer thus obtained was soluble in DMF, and gave IR absorptions at 1630, 985, and 910 $\mathrm{cm^{-1}}$, which are characteristic absorptions of vinyl group, and no absorptions around 2300 and 2900 $\mathrm{cm^{-1}}$. These results indicate that the polymerization of VI proceeded exclusively through the isocyanate group. The further polymerization of the residual functional group in the polymer obtained from VI was then examined in order to get a ladder polymer. However, the radical polymerization of the pendant vinyl group in the isocyanate polymer failed, since the isocyanate polymer was readily degraded in DMF at room temperature. The anionic polymerization of the isocyanate group in the vinyl polymer could not be carried out either because of insolubility of the vinyl polymer.

Copolymerization. Compounds II, III, and VI were submitted to copolymerization with styrene. The monomer reactivity ratios of these compounds were obtained by the intersecting

---

5) C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, **67**, 2250 (1945).

6) S. H. Merrill, *J. Org. Chem.*, **26**, 1301 (1961).

7) P. Jäger and E. S. Waight, *J. Chem. Soc.*, **1963**, 1339.

8) N. A. Adrova and K. K. Khomenkova, *Zh. Obshch. Khim.*, **32**, 2267 (1962).

9) E. L. Kropa and A. S. Nyquist, U. S. Pat. 2468713 (1949).

10) V. E. Shashoua, W. Sweeny and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).

TABLE 1. PHYSICAL PROPERTY AND IR SPECTRA

Compound	mp, °C (bp, °C)	IR Spectra cm^{-1}
II	(115.5—116.5/0.1 mmHg)	1718, 1629, 1608, 1402, 1342, 1275, 1176, 1102, 1011, 987, 907 856, 839, 779, 708
III	(69.5—70.0/0.1 mmHg)	1770, 1730, 1632, 1604, 1405, 1210, 1180, 988, 922, 873, 850, 768
IV	186.0—186.5	3300, 1653, 1590, 1513, 1498, 1323, 1150, 1098, 1087, 975, 910 835, 813, 770, 685
V	54.0—54.5	2180, 1681, 1630, 1605, 1401, 1250, 1188, 1113, 989, 930, 912, 855, 778, 768, 691
VI	(40.5—41.5/0.1 mmHg)	2290, 1630, 1605, 1522, 1108, 988, 910, 893
VII	95.5—97.0	3330, 1698, 1611, 1585, 1525, 1403, 1308, 1228, 1060, 984, 904 858, 833, 782, 761
VIII	108.0—108.5	3320, 1673, 1636, 1615, 1590, 1535, 1403, 1335, 1250, 1150, 997, 988, 900, 872, 831

TABLE 2. RADICAL POLYMERIZATION

Monomer g	Solvent m*l*	Time hr	Temperature °C	Yield g	η*
II 1.5	Dioxane 0.3	2	51	1.0	1.00**
III 0.8	Dioxane 0.5	4	75	0.7	—
IV 0.5	Acetone 3.0 DMF 2.0	11	70	0.35	0.16
VI 0.5	Toluene 2.0	0.5	60	0.3	—
VII 0.5	Dioxane 1.0	3	60	0.05	0.39
VIII 0.55	Dioxane 1.0	0.5	55	0.05	0.10***

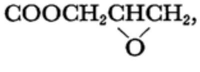
* η_{inh} in DMF (C=0.2 g/d*l*) at 30.0°C.
** [η] in DMF at 30.0°C
*** accompained with gel formation

TABLE 3. REACTIVITY RATIO AND *Q*, *e* VALUE

M_2	r_1	r_2	Q_2	e_2	Temp., °C
II	0.40±0.02	0.95±0.10	1.14	0.18	70.0
III	0.17±0.03	1.80±0.20	2.46	0.28	60.0
VI	0.75±0.10	1.10±0.10	0.94	−0.36	60.0

M_1=Styrene

method[11] from the compositions of the monomer feeds and copolymers obtained. The compositions of the copolymers were determined by analysis of the epoxy group for the copolymer from II, by analysis of chlorine for the copolymer of III, and by elemental analysis of nitrogen for VI. The monomer reactivity ratios and Alfrey-Price's *Q* and *e* values are shown in Table 3. The copolymer composition curves of styrene (M_1) with compounds II, III, and VI are shown in Fig. 1, where the mol% of m_1 in the copolymers is plotted against the mol% of M_1 in the monomer feeds.

The compounds II, III, and VI have electron-withdrawing groups, that is,  $\mathrm{COOCH_2\underset{O}{CHCH_2}}$, COCl, and NCO. It has been reported that, on the copolymerization of styrene (M_1) with *p*-substituted styrenes, there is a good linear relation between log(1/r_1) and σ^-,[12] or between log(1/r_1) and σ, using a modification of Hammett's equation.[13] *e* values have also been said to show polarity, and to have some correlation with σ in substituted ethylenes.[14] When the *e* values of *p*-substituted styrenes were plotted against the σ values for substituents, a good linear correlation was observed, as is shown in Fig. 2. The *e* and σ values are taken from Perrin's and Young's

---

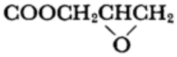
[11] G. E. Ham, "Copolymerization," ed. by G. H. Ham, Interscience Publishers, New York (1964), p. 29.

[12] C. Walling, E. R. Briggs, K. B. Walfstein and F. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

[13] M. Imoto, M. Kinoshita and M. Nishigaki, *Makromol. Chem.*, **94**, 238 (1966).

[14] J. Furukawa and T. Tsuruta, *J. Polymer Sci.*, **36**, 275 (1959).

TABLE 4. SPECTRA DATA

Compound	UV λ_{max} (ε) mμ	NMR τ(ppm) phenyl	vinyl	Substituent	σ
VI	259 (1.6×10^4)	2.81 2.93 3.10 3.23	3.14 3.32 3.41 3.58 4.17* 4.46* 4.64* 4.83*	NCO	0.27
II	268 (1.9×10^4)	1.94 2.08 2.54 2.68	3.03 3.21 3.32 3.50 4.02* 4.32* 4.57* 4.75*	 $\mathrm{COOCH_2\underset{\diagdown O \diagup}{CHCH_2}}$	0.64
III	280 (1.5×10^4)	2.18 2.30 2.70 2.82	3.11 3.27 3.38 3.55 3.98* 4.26* 4.45* 4.63*	COCl	0.71

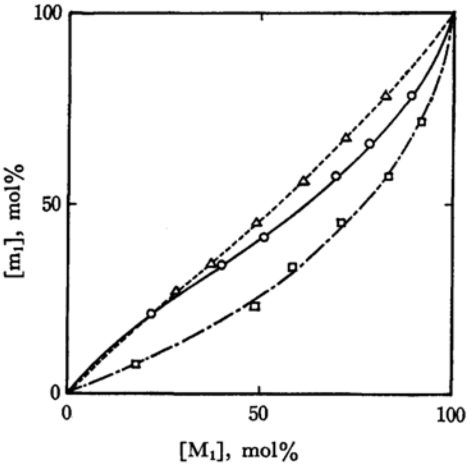
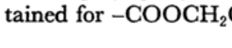


Fig. 1. Copolymer composition curves.
○ styrene (M_1)−II (M_2)
□ styrene (M_1)−III (M_2)
△ styrene (M_1)−VI (M_2)
Lines are calculated from the monomer reactivity ratios and spots are from experimental data.

tables[15,16] respectively.

When the σ values for the substituents of compounds II, III, and VI were estimated from the e-σ map (Fig. 2). The following values were obtained for  $-\mathrm{COOCH_2\underset{\diagdown O \diagup}{CHCH_2}}$, $-$COCl, and $-$NCO: 0.64, 0.71, and 0.27.

The σ value for *p*-NCO has been reported to be 0.24,[17] which is close to the estimated value of 0.27. The σ value for *p*-COCl can be estimated by Charton's method.[18] If X denotes a substituent with a known σ constant and Y an intervening group, the σ constant for the XY group can be estimated by the equation: $\sigma_{XY}=\alpha+\beta\sigma_X$. In this case, X=CO and Y=H, OCH_3, NH_2, and OH. The σ value given for *p*-COCl is 0.70, which is almost the same value as the estimated

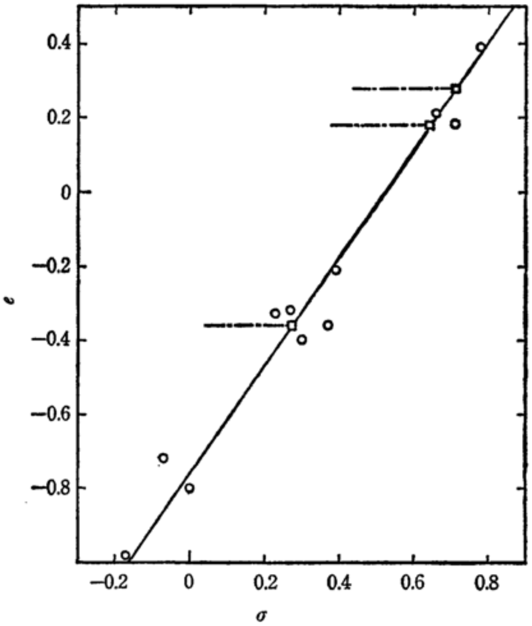


Fig. 2. Correlation between e and σ.
○ announced value[15,16]
□ this experiment

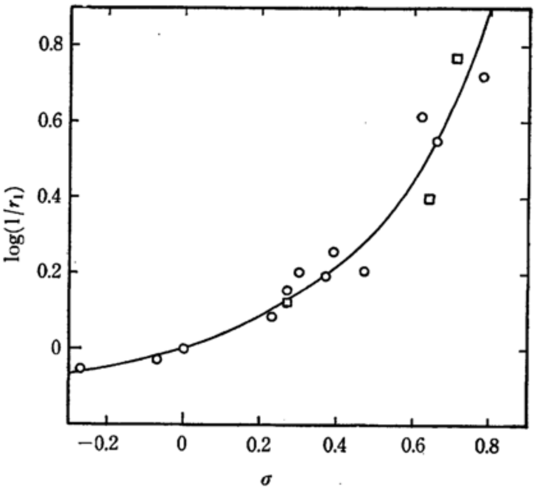


Fig. 3. Relationship between log(1/r_1) and Hammett's σ.
○ announced value[15,16]
□ this experiment

---

[15] J. Clark and D. D. Perrin, *Quart. Reviews,* **18**, 295 (1964).

[16] L. J. Young, *J. Polymer Sci.,* **54**, 411 (1961).

[17] J. H. Saunders and K. C. Frisch, "Polyurethanes," Interscience Publishers, New York (1962), p. 144.

[18] M. Charton, *J. Org. Chem.,* **28**, 3121 (1963).

value, 0.71. If the α and β values calculated by Charton are used, the σ value may be 0.60, but the Y groups used by him include substituent of a different type (COO^-), which deviates from the equation given above, and so the error must be much greater. The σ value for the glycidyl ester has not yet been obtained. The value obtained here is a little higher than the value for $-COOC_2H_5$, 0.45.[15] This can be attributed to the inductive effect of oxygen in a three-membered ring. The λ_{max} in UV and τ values in NMR for $CH_2=$ (asterisked value) of these three monomers show an orderly correlation with the σ value assumed here (Table 4). The values of $\log(1/r_1)$ are plotted against σ in Fig. 3. This figure also shows that the σ values obtained here are reasonable, because the cubic points (our results) are almost on the plotted curve.

Experimental

Monomers. *Glycidyl p-Vinylbenzoate (II).* *p*-(β-Bromoethyl)benzoic acid was prepared from *p*-(β-bromoethyl)acetophenone by the procedure of Foreman,[19] using sodium hypochlorite (antiformine). Potassium *p*-vinylbenzoate (I) was obtained by heating *p*-(β-bromoethyl)benzoic acid with potassium hydroxide and hydroquinone in ethanol. Finely-powdered crude I (15.0 g), epichlorohydrin (120 m*l*), triethylbenzylammonium chloride (150 mg), and hydroquinone (80 mg) were heated while being stirred under reflux for 30 min. The resulting potassium chloride was filtered, and the excess epichlorohydrin was removed under reduced pressure. The fractional distillation of the residue gave 7.2 g (67%) of a colorless product; bp 115.5—116.5°C/0.1 mmHg. The epoxide content was over 99.0% (HCl-dioxane method[20]). $n_D^{20}=1.5622$.

Found: C, 70.63; H, 6.01%. Calcd for $C_{12}H_{12}O_2$: C, 70.57; H, 5.92%.

p-Vinylbenzoyl Chloride (III). To a mixture of *p*-vinylbenzoic acid (10.0 g) and *p*-*t*-butylpyrocathecol (10 mg), a 20 m*l* portion of thionyl chloride was added under cooling. The reaction mixture was kept below 10°C for 5 hr, and then gradually warmed to 40°C and maintained there for 1 hr. After the removal of the thionyl chloride, distillation gave 8.8 g (78%) of colorless liquid; bp 69.5—70.0°C/0.1 mmHg. $n_D^{20}=1.6020$.

The reaction of *p*-vinylbenzoic acid (10.0 g) with a large excess of thionyl chloride (60 m*l*) gave a product (bp 90—100°C/1 mmHg) which solidified on standing; recrystallization from *n*-hexane gave white needles which melted at 86.0—86.5°C.

IR: 1760, 1601, 1410, 1208, 1170, 933, 885, 847, 808 cm^{-1}

NMR: 2.04, 2.17, 2.62, 2.74 (quartet) and 3.15 (singlet)

Found: C, 53.65; H, 3.24; Cl, 34.57%. Calcd for $C_9H_6OCl_2$: C, 53.50; H, 3.00; Cl, 35.09%.

From these data, the product was identified as *p*-(α-chlorovinyl)benzyol chloride.[21]

p′-β-Chloroethylaminosulfonyl-p-vinylbenzanilide (IV). *N*-β-Chloroethylsulfoanilamide (2.6 g) and triethylamine (1.2 g) were dissolved in a mixture of acetone (3 m*l*) and ether (10 m*l*). To this solution acid chloride III (1.9 g) was added, drop by drop, on cooling in an ice-salt bath. In an hour of stirring a white precipitate appeared. The product was filtered, washed with water, and dried. It weighed 3.0 g (75%). Recrystallization from benzene-ethanol gave white crystals; mp 186.0—186.5°C.

Found: C, 56.14; H, 4.70; N, 7.62%. Calcd for $C_{17}H_{17}N_2O_3ClS$: C, 55.98; H, 4.70; N, 7.68%.

p-Vinylphenyl Isocyanate (VI). To a solution of sodium azide (10.0 g) in distilled water (26 m*l*), there was added, drop by drop, a solution of III (8.3 g) in ether (7 m*l*) at a temperature around 0°C. The mixture was then agitated for 30 hr at 0°C. The *p*-vinylbenzazide V thus deposited was filtered, washed thoroughly with water and then with a small amount of *n*-hexane, and dried. It weighed 8.0 g (93%); mp 54.0—54.5°C (recrystallized from *n*-hexane).

A solution of V (8.0 g) in toluene was gradually heated; gas evolved about 80°C. The solution was then refluxed for 30 min. After the removal of the toluene, the distillation of the residual liquid gave a colorless liquid, 4.4 g (66%); bp 40.5—41.5°C/0.1 mmHg. $n_D^{20}=1.5785$. This product gave methyl *p*-vinylcarbanilate by a reaction with methanol; mp 85.5—86.5°C (recrystallized from ether-petroleum ether).

Found: N, 7.68%. Calcd for $C_{10}H_{11}NO_2$: N, 7.91%.

Glycidyl p-Vinylcarbanilate (VII). This compound was obtained by the reaction of VI with glycidol in ether. The yield was 96%; mp 95.5—97.0°C (recrystallized from benzene-*n*-hexane).

Found: C, 65.42; H, 5.92; N, 6.32%. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39%.

N-p-Vinylphenyl-N′, N′-ethyleneurea (VIII). This compound was obtained by the reaction of VI with aziridine in cooled ether. The yield was 70%; mp 108.0—108.5°C (recrystallized from aqueous methanol).

Found: C, 69.83; H, 6.17; N, 14.74%. Calcd for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43; N, 14.88%.

Polymerization. *Radical Polymerization.* The radical polymerization was carried out with an appropriate solvent in a sealed ampule using AIBN as the initiator. The polymer was obtained by pouring the reaction mixture into methanol (for II, IV, VII, and VIII) or into anhydrous *n*-hexane (for III and VI). The viscosities were measured in a DMF solution at 30.0°C.

Anionic Polymerization. The procedure for the anionic polymerization of VI was the same as that described by Shashoua.[10] The yield of the polymer was 32%. If the polymer obtained was dissolved in DMF at room temperature, it was degraded to a cyclic trimer and symmetrical urea. Therefore, the viscosity of the isocyanate polymer could not be obtained. Radical polymerization by the high dilution of this polymer in DMF failed for the same reason.

Copolymerization. Two grams of a pair of monomers and 10 mg of AIBN were mixed in a sealed tube under nitrogen. The polymerization was then carried out at a fixed temperature. The conversion of the copolymer was less than 8%. The resulting polymer was

---

[19] E. L. Foreman and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1435 (1940).

[20] G. King, *Nature*, **164**, 1106 (1949).

[21] W. K. Detweiler and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2882 (1950).

precipitated with *n*-hexane, dried under a vacuum, and submitted to the analysis of the epoxy group[20] or to elemental analysis.

Spectra Analyses. The infrared spectra were obtained with a Hitachi Model EPI-2 double-beam spectrometer. The NMR spectra were measured at room temperature with a Japan Electron Optics Laboratory C-60 spectrometer. The UV spectra were measured in an *n*-hexane solution with a JASCO ORD/UV-5 spectrometer.

The authors wish to express their thanks to the Nissō Kakō Co., Ltd., for kindly supplying the starting materials.