Syntheses of Saccharin and Cyclamate Derivatives Bearing Polymerizable Vinyl Group

Hiroyoshi KAMOGAWA,* Shuji YAMAMOTO, and Masato NANASAWA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu, Yamanashi 400

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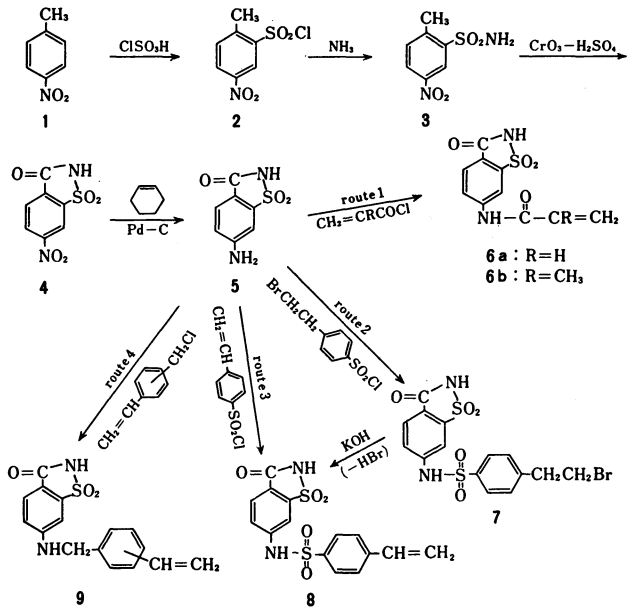
Vinyl monomers containing saccharin or cyclamate residues were synthesized. 6-Acrylamido-, 6-methacrylamido-, 6-(4-styrenesulfonamido)-, and 6-(vinylbenzylamino)saccharins were synthesized from 6-aminosaccharin. *N*-[2-(4-Styrenesulfonamido)cyclohexyl] and *N*-[2-(vinylbenzylamino)cyclohexyl]sulfamic acids were synthesized starting with 1,2-cyclohexanediamine *via* sodium *N*-(2-aminocyclohexyl)sulfamate. All monomers thus synthesized were found to polymerize or copolymerize with *N*-vinyl-2-pyrrolidone to afford vinyl polymers with pendant saccharin and cyclamate units.

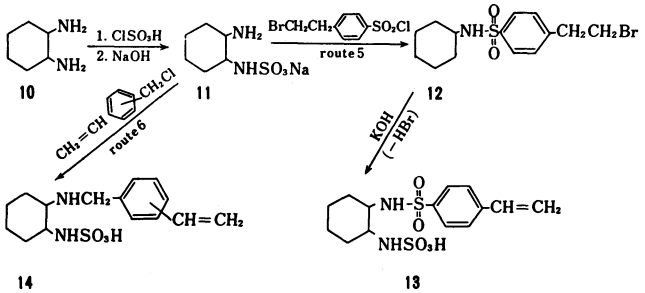
In our previous studies, we have prepared food colorant monomers[1] and food preservative and antioxidant monomers and their polymers,[2,3] which are considered to have a potentiality as nondigestive and nonabsorbable food additives.

In this paper, we wish to report syntheses of vinyl monomers containing saccharin and cyclamate residues, which are intended to provide nondigestive sweeteners in their final polymer forms.

Saccharin monomers (**6a**, **6b**, **8**, **9**) were synthesized *via* the key intermediate 6-aminosaccharin (**5**) as follows:



Cyclamate vinyl monomers (**13**, **14**) were synthesized *via* sodium *N*-(2-aminocyclohexyl)sulfamate (**11**) in the following manners:



All monomers synthesized were homopolymerized or copolymerized with *N*-vinyl-2-pyrrolidone (VP) to afford respective pendant polymers.

Results and Discussion

Owing to the deactivating effect of *p*-nitro group on 3 and 5 positions of *p*-nitrotoluene (**1**), 2-methyl-5-nitrobenzenesulfonamide (**3**) was isolated as the sole product (^{1}H NMR) by the chlorosulfonation of **1** and subsequent reaction with ammonia. Chromium trioxide oxidation in sulfuric acid was adopted for the conversion of **3** to 6-nitrosaccharin (**4**), since permanganate oxidation as in the case of commercial production of saccharin gave no satisfactory results (very low yields). For the reduction of the nitro group of **4** to afford 6-aminosaccharin (**5**) the amphoteric character of **5** hindered the use of conventional methods such as the $SnCl_2$–HCl one. The combination of cyclohexene as hydrogen donor with Pd–C as catalyst[4] allowed a smooth progress of reduction and easy purification of the product **5** by reprecipitation. 6-Acrylamido- and 6-methacrylamidosaccharins (**6a** and **6b**) were synthesized by the reactions of **5** with acryloyl chloride and methacryloyl chloride in aqueous mixtures, respectively (route 1). Alternatively, **6a** was synthesized from **4** by the reduction with aqueous sodium dithionite and subsequent addition of acryloyl chloride to the reaction mixture without isolating **5**, although yield was low (*ca.* 13%). The sulfonamide group which is more resistant to hydrolysis was introduced by the reaction of **5** with 4-(2-bromoethyl)benzenesulfonyl chloride (route 2). The presence of acidic hydrogen (s, 1H) at δ 11.5 in NMR identified structure **7**. The dehydrobromination of **7** by a conventional procedure gave a vinyl monomer **8**. Monomer **8** was also prepared from **5** in a single step by the use of *p*-vinylbenzenesulfonyl chloride (route 3). The reaction of **5** with vinylbenzylchloride (*m*/*p*=60/40) provided another vinyl monomer 6-(vinylbenzylamino)saccharin (**9**, a *m*-*p* mixture) (route 4). Single absorption peak (NH) at 3380 cm^{-1} in IR (KBr) identified structure **9**. Both column and thin-layer chromatographic separations of meta from para isomer failed due largely to the unfavorable solubility characteristic of **9**.

In the cyclamate series, 1,2-cyclohexanediamine (**10**) was converted to sodium *N*-(2-aminocyclohexyl)sulfamate (**11**), which was subjected to the same reaction procedures as those in the saccharin series using 4-(2-

Table 1. Polymerization behavior of the synthesized monomers

No.	Monomer	VP/Monomer (mol/mol)	Polymer		
			Conversion %	VP/Monomer[a] (mol/mol)	$[\eta]$ dl g^{-1}
1	**6a**	0	85	0	0.34
2	**6a**	8.99	35	13.9	0.78
3	**6b**	0	56	0	0.18
4	**6b**	10.03	28	5.00	0.18
5	**8**	0	82	0	0.13
6	**8**	8.92	13	0.61	0.07
7	**9**	0	68	0	Insol in DMF
8	**9**	13.24	38	0.045	Insol in DMF
9	**13**	0	72	0	Insol in DMF
10	**13**	8.96	44	1.87	Insol in DMF
11	**14**	9.04	34[b]	13.3	0.39[c]

a) Determined by CHN-analyses. b) A solution of **14** (0.21 g), VP (0.68 g), potassium persulfate (0.009 g), and sodium hydroxide (0.033g) in water (3 ml) was polymerized. c) Value in water.

bromoethyl)benzenesulfonyl chloride and vinylbenzyl chloride to afford *N*-[2-[4-(2-bromoethyl)benzenesulfonamido]cyclohexyl]sulfamic acid (**12**) and *N*-[2-(vinylbenzylamino)cyclohexyl]sulfamic acid (**14**), respectively (routes 5 and 6). Compound **12** was converted to the corresponding vinyl monomer **13** by alkaline dehydrobromination. Relatively low yields observed in steps **12**→**13** and **11**→**14** (35% and 29%) are considered to be caused by the fact that fairly large amounts of the sulfamic acids produced remained in solutions without being isolated. All attempts to separate para and meta isomers of **14** failed too.

Some of the novel monomers synthesized here are slightly colored, presumably due to the presence of traces of unremovable impurities. However, results of IR, NMR, MS, and elemental analyses indicate that they are essentially pure.

As indicated in Table 1, all monomers were found to polymerize in either *N*,*N*-dimethylformamide (DMF) or aqueous alkali (No. 11 in Table 1) with radical initiators. Some homopolymers and copolymers with *N*-vinyl-2-pyrrolidone (VP) (Nos. 7—10) were insoluble in DMF. These monomers (**9**, **13**), however, can make alkali-soluble copolymers by selecting suitable monomer ratios, as exemplified in the case of monomer **14** (No. 11). It is interesting to note that both saccharin and cyclamate monomers with the sulfonamide linkage (**8** and **13**) provide remarkably low values of VP/monomer ratio in copolymer as compared with those in the corresponding monomers (Nos. 6 and 10). This is also the case with monomer **9** having the benzylamino linkage (No. 8). In the latter two cases (monomers **9** and **13**), however, the polymerizations were heterogeneous, so that exact estimation of monomer reactivity may be difficult.

All copolymers of saccharin and cyclamate monomers with VP synthesized here can be made water-soluble, when suitable monomer ratios are selected and the resulting copolymers are neutralized with aqueous alkali. Although the taste of these copolymers has not exactly been estimated at this stage, copolymers of this kind, as they are or when suitably modified, might conform to the requirements mentioned above.

Experimental

IR, ^{1}H NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Hitachi RMU-6 MG spectrometer, respectively. Elemental analyses were conducted using a Perkin-Elmer 250 instrument.

2-Methyl-5-nitrobenzenesulfonamide (3). A solution of *p*-nitrotoluene (6.9 g, 50 mmol) in chlorosulfuric acid (17.5 g, 150 mmol) was kept at 60—70 °C for 24 h with exclusion of moisture. The reaction mixture was poured onto ice and extracted with ether (200 ml). The organic layer was washed with aqueous sodium chloride, treated with concd aqueous ammonia (50 ml), and stirred by the application of heat to evaporate ether completely (about 2 h). The mixture was then filtered and crude product was recrystallized from water to afford yellow needles (mp 183—185 °C) in 45% yield. Found: C, 38.73; H, 3.58; N, 13.10%. Calcd for $C_7H_8N_2SO_4$: C, 38.89; H, 3.73; N, 12.96%. IR (KBr) 3420, 3300 (NH_2), 1600 (Ar), 1540 (NH), 1350 (NO_2), 1330, 1310 (SO_2), 1160, and 1120 (SO_2) cm^{-1}. NMR ($CDCl_3$–DMSO-d_6) δ=2.8 (s, 3H, Me), 7.4—7.8 (d, 3H, NH_2+ArH), 8.3 (d, 1H, ArH), and 8.8 (s, 1H, ArH). MS (*m/e*) 216 (M^+, 8) and 135 (100).

6-Nitrosaccharin (4). To a solution of chromium trioxide (9.0 g, 900 mmol) in water (66.7 ml) concd sulfuric acid (83.5 ml) was added gradually. To the resulting solution was added **3** (4.32 g, 20 mmol) and the mixture was stirred at room temperature for 24 h. Crude product was obtained by filtration of the reaction mixture with a glass filter followed by thorough washing with water. Purification by dissolution in 10% aqueous sodium hydrogencarbonate, filtration, and reprecipitation of the filtrate with 5% aqueous hydrochloric acid provided a white powder (mp 205—207 °C) in 56% yield. Found: C, 36.54; H, 1.89; N, 12.12%. Calcd for $C_7H_4N_2SO_5$: C, 36.85; H, 1.78; N, 12.28%. IR (KBr) 3150 (NH), 1730 (C=O), 1660 (Ar), 1530 (NO_2), 1340 (SO_2, NO_2), 1170, and 1120 (SO_2) cm^{-1}. NMR ($CDCl_3$–DMSO-d_6) δ= 8.1—9.0 (m, 3H, ArH), 10.1 (s, 1H, NH). MS (*m/e*) 228 (M^+, 100).

6-Aminosaccharin (5). To a solution of **4** (11.4 g, 50 mmol) and cyclohexene (25.4 ml, 250 mmol) in ethanol (100 ml), 5% Pd–C (53.0 g) was added with cooling. The black mixture was refluxed for 2 h with stirring and filtered several times until the filtrate became clear. The filtrate was then evaporated to dryness to afford a crude product, which was purified by dissolution in 2 M hydrochloric acid (1 M=1 mol dm^{-3}) and subsequent precipitation into aqueous sodium

hydrogencarbonate to provide a slightly yellow powder (mp 264—265 °C) in 63% yield. Found: C, 42.46; H, 3.22; N, 13.98%. Calcd for $C_7H_6N_2SO_3$: C, 42.42; H, 3.05; N, 14.13%. IR (KBr) 3380, 3320 (NH), 1720 (C=O), 1610 (Ar), 1315, 1170, and 1120 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ= 6.5—7.8 [m, 3H (Ar)+3H (NH)]. MS (*m/e*) 198 (M^+, 54) and 63 (100).

*6-(Acrylamido)saccharin (**6a**).* *(a) From 6-Aminosaccharin (**5**):* To a solution of **5** (1.98 g, 10 mmol), sodium hydrogencarbonate (1.8 g), and a small amount of hydroquinone in water (50 ml), acryloyl chloride (2.72 g, 30 mmol) was added dropwise with ice cooling followed by stirring at room temperature for 30 min. The reaction mixture was then poured into cold 2 M hydrochloric acid to effect precipitation. The precipitate was filtered and recrystallized from methanol to afford a slightly yellow powder (mp>290 °C) in 73% yield. Found: C, 47.62; H, 3.28; N, 11.09%. Calcd for $C_{10}H_8N_2SO_4$: C, 47.62; H, 3.20; N, 11.11%. IR (KBr) 1735 (C=O), 1695 (amide I), 1600 (Ar), 1530 (amide II), 1320, 1180, 1150 (SO_2), 980, and 900 (CH_2=CH–) cm^{-1}. NMR (DMSO-d_6) δ=5.8—6.0 (m, 1H, –C<u>H</u>=CH_2), 6.3—6.5 (t, 2H, –CH=C<u>H</u>$_2$), 7.9 (s, 2H, ArH), 8.5 (s, 1H, ArH), 9.7 (s, 1H, amide NH), and 10.9 (s, 1H, =NH). MS (*m/e*) 252 (M^+, 20) and 55 (100).

*(b) From 6-Nitrosaccharin (**4**):* To a solution of sodium dithionite (3.5 g, 22 mmol) in water (5 ml), **4** (1 g, 4 mmol) was added and the mixture stirred at room temperature for 30 min. A small amount of sodium hydrogencarbonate was added to give a clear solution, which was cooled in an ice-water bath followed by addition of a small amount of hydroquinone. Acryloyl chloride (1.2 g, 13 mmol) was then added dropwise to the solution and the mixture was stirred for 30 min under ice cooling. Acidification of the solution with 5% hydrochloric acid provided a crude product, which was purified by dissolution in 10% aqueous sodium carbonate and subsequent precipitation into 5% hydrochloric acid to afford a slightly green powder (**6a**) in 13% yield. Elemental analyses, IR, NMR, and MS identified the same structure as that prepared in *(a)*.

*6-(Methacrylamido)saccharin (**6b**).* The same reaction procedure as that for **6a** was applied to **5** (2.0 g, 10 mmol) and methacryloyl chloride (3.1 g, 30 mmol) to afford a slightly yellow powder (mp 215—217 °C) in 71% yield. Found: C, 49.92; H, 3.90; N, 10.01%. Calcd for $C_{11}H_{10}N_2SO_4$: C, 50.25; H, 3.89; N, 9.85%. IR (KBr) 1760 (C=O), 1710 (amide I), 1590 (Ar), 1540 (amide II), 1340, 1190, 1130 (SO_2), and 930 (CH_2=CCH_3–) cm^{-1}. NMR (DMSO-d_6) δ=2.1 (s, 3H, Me), 5.7 (s, 1H, =CH_2), 6.0 (s, 1H, =CH_2), 8.0—8.8 (m, 3H, ArH), 8.6 (s, 1H, NH), and 10.6 (s, 1H, NH). MS (*m/e*) 266 (M^+, 5) and 69 (100).

*6-[4-(2-Bromoethyl)benzenesulfonamido]saccharin (**7**).* To a solution of **5** (2.0 g, 10 mmol), a small amount of hydroquinone and sodium hydroxide (0.96 g) in water (30 ml) was added with stirring a solution in acetonitrile (25 ml) of 4-(2-bromoethyl)benzenesulfonyl chloride (5.7 g, 20 m mol),prepared from (2-bromoethyl)benzene and chlorosulfuric acid according to a known method.[5] The mixture was stirred at room temperature for 12 h and poured into cold 2 M hydrochloric acid to afford a precipitate, which was filtered and recrystallized from methanol–water to afford a slightly pink powder (mp 168—171 °C) in 27% yield. Found: C, 40.51; H, 3.05; N, 6.25%, Calcd for $C_{15}H_{13}N_2S_2BrO_5$: C, 40.46; H, 2.94; N, 6.29%. IR (KBr) 3240 (NH), 2920, 2850 (CH_2), 1730 (C=O), 1325, and 1160 (SO_2) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$) δ=3.1—3.4 (t, 2H, CH_2), 3.7—3.9 (t, 2H, CH_2), 6.3 (s, 1H, NH), 7.5—8.2 (m, 7H, ArH), and 11.5 (s, 1H, NH). MS (*m/e*) 216 and 197.

*6-(4-Styrenesulfonamido)saccharin (**8**).* *(a)* Via *Route 2*: A solution of **7** (2.0 g, 4.5 mmol), potassium hydroxide (0.6 g, 11 mmol), and a small amount of hydroquinone in methanol (30 ml) was refluxed for 1 h with stirring. The reaction mixture was poured into cold 2 M hydrochloric acid. The precipitate thus produced was filtered and recrystallized from methanol–water to afford a slightly pink powder (mp 144—147 °C) in 80% yield. Found: C, 49.56; H, 3.12; N, 7.50%. Calcd for $C_{15}H_{12}N_2S_2O_5$: C, 49.44; H, 3.32; N, 7.69%. IR (KBr) 1730 (C=O), 1320, 1160 (SO_2), 985, and 910 (vinyl) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$) δ=5.2—6.2 (q, 2H, CH_2=), 6.3 (s, 1H, NH), 6.5—7.3 (m, 1H, =CH–), 7.5—8.1 (m, 7H, ArH), and 11.6 (s, 1H, NH).

(b) Via *Route 3*: A solution of **5** (2.0 g, 10 mmol), *p*-vinyl benzenesulfonyl chloride (4.1 g, 20 mmol),[6] triethylamine (1.5 g), and hydroquinone (0.1 g) in DMF (50 ml) was stirred at room temperature for 12 h and poured into cold 2 M hydrochloric acid. The resulting precipitate was collected by filtration and washed with ether. Recrystallization from methanol–water provided a white powder (mp 148—149 °C) in 14% yield. Found: C, 49.19; H, 3.43; N, 7.47%. IR and NMR spectra were essentially identical with those of the product in *(a)*.

*6-(Vinylbenzylamino)saccharin (**9**).* A solution of **5** (1.0 g, 5 mmol), triethylamine (0.7 ml, 5 mmol), vinylbenzyl chloride (Seibi Chem. Co., *m/p*=60/40; 2.3 g, 15 mmol), and hydroquinone (0.1 g) in DMF (30 ml) was stirred at 90 °C for 7 h. The reaction mixture was poured into ice-cold 2 M hydrochloric acid. The resulting precipitate was filtered and recrystallized from methanol–water to afford a white powder (mp 155—158 °C) in 32% yield. Found: C, 61.33; H, 4.48; N, 8.70%. Calcd for $C_{16}H_{12}N_2SO_3$: C, 61.13; H, 4.49; N, 8.91%. IR (KBr) 3380 (NH), 2945, 2845 (CH_2), 1720 (C=O), 1600 (Ar), 1330, 1300, 1175, 1140 (SO_2), 995, and 915 (vinyl) cm^{-1}. NMR (DMSO-d_6+$CDCl_3$) δ=4.9 (s, 2H, CH_2), 5.3—6.1 (q, 2H, CH_2=), 6.7—8.0 (m, 10H, =CH–+ ArH+NH). MS (*m/e*) 314 (M^+, 4) and 250 (100).

*Sodium N-(2-Aminocyclohexyl)sulfamate (**11**).* To a solution of 1,2-cyclohexanediamine (**10**; 25 g, 220 mmol) in anhydrous chloroform (110 ml) cooled below 0 °C, chlorosulfuric acid (8.43 g, 72 mmol) was added dropwise with stirring. It required about 2 h. The mixture was further stirred for 30 min below 0 °C and poured into 6% aqueous sodium hydroxide (100 ml). The aqueous layer was separated, extracted with ether to remove the ether-soluble part, and free-zedried to afford a crude product, which was extracted with hot 90% ethanol to afford a white powder upon cooling in 53% yield. Found: C, 33.31; H, 6.23; N, 12.62%. Calcd for $C_6H_{13}N_2SO_3Na$: C, 33.33; H, 6.06; N, 12.96%. IR (KBr) 2940, 2860 (CH_2, CH), 1610 (NH), and 1200 (SO_2) cm^{-1}. NMR (D_2O) δ=1.0—3.0 (m, 11H, CH_2, CH+NH+NH_2).

*N-[2-[4-(2-Bromoethyl)benzenesulfonamido]cyclohexyl]sulfamic Acid (**12**).* A mixture of **11** (1.0 g, 4.6 mmol), 4-(2-bromoethyl) benzenesulfonyl chloride (1.57 g, 5.6 mmol), sodium hydroxide (0.22 g), and acetonitrile–water (1 : 2 v/v; 30 ml) was stirred at room temperature for 12 h. The reaction mixture was then poured into cold 2 M hydrochloric acid and let stand overnight to afford a white precipitate, which was filtered, washed with ether, dissolved in aqueous sodium hydroxide, and reprecipitated with hydrochloric acid to afford white crystals (mp 184—187 °C) in 74% yield. Found: C, 37.89; H, 4.82; N, 6.50%. Calcd for $C_{14}H_{21}N_2S_2BrO_5$: C, 38.09; H, 4.80; N, 6.35%. IR (KBr) 3290 (NH), 2960, 2950, 2870 (CH, CH_2), 1595 (Ar), 1330, 1315, 1300, 1165, and 1155 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ=0.8—1.9 (b, 8H, 4CH_2), 1.9—3.3 (b, 3H, 2CH+NH), 2.8—3.4 (t, 2H, CH_2), 3.5—4.0 (t, 2H, CH_2), 5.3 (s, 1H, NH), and 7.5—8.3 (q, 5H, ArH+SO_3H).

N-[*2-(4-Styrenesulfonamido)cyclohexyl*]*sulfamic Acid* (**13**). A mixture of **12** (1.5 g, 3.4 mmol), potassium hydroxide (0.42 g, 7.6 mmol), and hydroquinone (0.1 g) in 90% ethanol (30 ml) was stirred at 80 °C for 1 h. The resulting solution was poured into ice-cold 2 M hydrochloric acid to afford a precipitate, which was filtered, dissolved in aqueous sodium hydroxide, and reprecipitated with hydrochloric acid to afford a slightly pink powder (mp 148—149 °C) in 35% yield. Found: C, 46.54; H, 5.68; N, 7.86%. Calcd for $C_{14}H_{20}N_2S_2O_5$: C, 46.65; H 5.59; N, 7.77%. IR (KBr) 2935, 2865 (CH_2, CH), 1600 (Ar), 1320, 1160 (SO_2), 990, and 930 (vinyl) cm^{-1}. NMR ($CDCl_3$+DMSO-d_6) δ=0.8—1.9 (b, 8H, $4CH_2$), 2.0—3.5 (m, 3H, 2CH+NH), 5.5 (d, 1H, CH_2=), 6.0 (d, 1H, CH_2=), 6.8 (q, 1H, =CH–), 7.5—8.1 (q, 5H, ArH+NH), and 8.5 (s, 1H, $-SO_3H$).

N-[*2-(Vinylbenzylamino)cyclohexyl*]*sulfamic Acid* (**14**). To a solution of **11** (2.0 g, 9.3 mmol), triethylamine (1.1 g, 11 mmol), and hydroquinone (0.2 g) in 90% ethanol (30 ml), vinylbenzyl chloride (*m*/*p*=60/40; 1.41 g, 9.3 mmol) was added dropwise and the mixture stirred at 65 °C for 2 h. The reaction mixture was poured into cold 2 M hydrochloric acid. Upon standing overnight, the resulting precipitate was filtered and purified by dissolution in aqueous sodium hydroxide and subsequent reprecipitation into cold aqueous hydrochloric acid. A slightly colored powder of mp 255—257 °C was obtained in 29% yield. Found: C, 58.26; H, 7.06; N, 8.83%. Calcd for $C_{15}H_{21}N_2SO_3H$: C, 58.04; H, 7.14; N, 9.02%. IR (KBr) 3350 (NH), 2945, 2865 (CH_2, CH), 1630 (NH), 1600 (Ar), 1280, 1170 (SO_2), 985, and 925 (vinyl) cm^{-1}. NMR (CF_3COOH) δ=1.0—2.7 (b, 10H, CH_2, CH), 3.2—3.8 (b, 1H, NH), 4.1—4.8 (b, 3H, CH_2NH), 5.5 (d, 1H, CH_2=), 6.0 (d, 1H, CH_2=), 6.9 (q, 1H, =CH–), 7.0—8.0 (m, 4H, ArH), and 10.5 (s, 1H, $-SO_3H$).

Polymerization of Monomers. In a typical example, a solution of monomer **6a** (1.5 g) and α,α'-azobisisobutyronitrile (AIBN; 0.015 g) in DMF (3.5 g) was put into a glass ampoule, which was evacuated, filled with nitrogen, and sealed in a conventional manner. Polymerization was carried out at 70 °C for 72 h. The content of the ampoule was then poured into aqueous sodium carbonate and dialyzed through a cellulose tubing (Visking) against water for 3 d. The dialyzed mixture was filtered and the filtrate was freeze-dried.

In the copolymerization with VP, the composition was adjusted so as to afford 30% total monomer concentration and 1% AIBN/total monomers. The results thus obtained are given in Table 1.

All homopolymers and copolymers synthesized indicated IR absorptions at 2930 and 2860 cm^{-1} characteristic of the vinyl polymer backbone together with those of the pendant saccharin and cyclamate units.

Intrinsic Viscosity. Intrinsic viscosities [η] of the synthesized polymers were measured in DMF solutions at 20 °C by means of an Ostwald-type viscometer, unless otherwise noted.

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