Vinyl Polymers Bearing Pyrrole Ring: I. Syntheses of Pyrroles Having 3-Substituent Bearing Vinyl Group

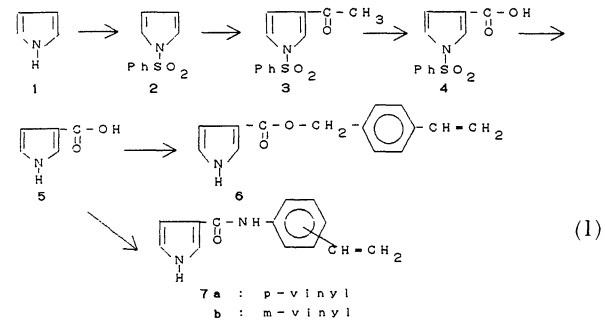
Hiroyoshi KAMOGAWA,* Takuharu NAKATA, Shin OHORI, and Sei KOMATSU
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400
(Received November 14, 1990)

Synopsis. Pyrroles having 3-substituent bearing the vinyl group with an ester or amide spacer were synthesized starting with 1-(phenylsulfonyl)pyrrole. Homopolymerization of the vinyl monomers thus synthesized provided cross-linked insoluble polymers, but their copolymers with 1-vinyl-2-pyrrolidone were soluble in common solvents.

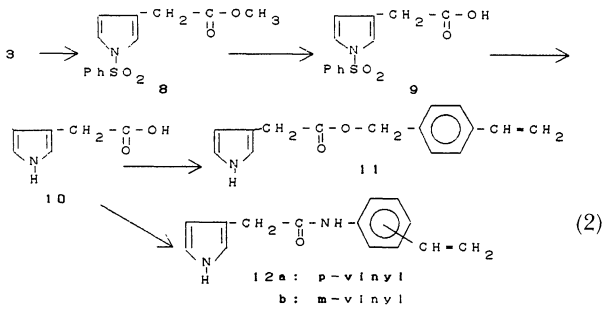
3-Substituted pyrroles have been little synthesized, since, in pyrrole, 2-position is the most reactive for electrophilic attacks such as preparation of 5,10,15,20,-tetraphenylporphyrins and polymerization.[1)]

In the present note, we wish to report the first synthesis of pyrroles having 3-substituent bearing a vinyl group. Accordingly, 3-substituted pyrroles reactive in both vinyl group and the 2-position of the pyrrole ring were obtained and their free-radical polymerization characteristics were investigated.

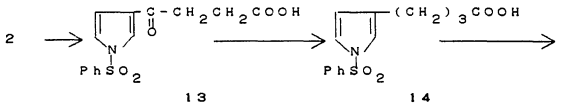
Pyrroles bearing a styrenic double bond **6** and **7a,b**, **11** and **12a,b**, and **16** and **17a,b**, were synthesized taking advantage of a high electrophilic reactivity at the 3 position of the pyrrole ring of **2** according to Eqs. 1, 2, and 3, respectively.

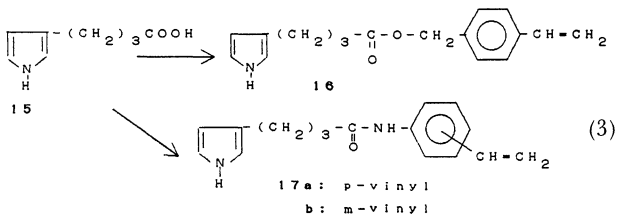


(1)



(2)





(3)

Results and Discussion

Vinyl monomer **6** was prepared by the reaction of **5**, synthesized following the route shown in Eq. 1, with *p*-vinylbenzyl chloride in DMF in the presence of triethylamine (TEA) as HCl-acceptor. Amide monomers **7a** and **7b** were prepared also by treatment of **5** with methyl chloroformate in the presence of TEA to afford a mixed anhydride, followed by addition of *p*- and *m*-vinylanilines.

Vinyl monomers **11** and **12a,b** were synthesized following the route shown in Eq. 2 in the same manners as those for **6** and **7a,b**. The last synthesis of monomers bearing a trimethylene group (**16** and **17a,b**) consisted of the application of the same ester and amide formation procedures as those for **6** and **7a,b** to **15**, synthesized following the route shown in Eq. 3. Ester and amide monomers thus prepared were subjected to free radical polymerization under conventional conditions. The results thus obtained are summarized in Table 1.

It is known from this Table 1 that homopolymerization only afforded cross-linked insoluble polymers for all monomers (Exp. Nos. 1—9), indicating that the reactive 2-position of the pyrrole ring of the monomer and/or the resulting polymer reacted each other during polymerization. Thus, copolymerizations with a large excess of 1-vinyl-2-pyrrolidone (VP) (Exp. Nos. 10—15) were carried out to provide soluble polymers, although their molecular weights, as judged from the values of intrinsic viscosity [η], and conversions were low, as was often the case with copolymerization of VP.[2)]

Conversions for *m*-vinyl polymers (Exp. Nos. 11, 13, and 15) were higher than those for *p*-vinyl ones (10, 13, and 15). In IR spectra, absorptions at 990 and 910 cm^{-1}, attributable to the vinyl group, no longer exist and a large absorption around 1650 cm^{-1}, due to the VP portion in polymer, is discernible, thereby indicating that polymerization took place.

In conclusion, it can be said generally that, by copolymerization of the monomers synthesized as above, vinyl polymers bearing the pyrrole ring as pendant of polymer molecular chain are obtained

Table 1. Polymerization Behavior of Ester and Amide Monomers[a]

Expt No.	Monomer M	VP/M mol/mol	Polymer Conversion	Polymer Solubility	Polymer $[\eta]$[b] dl g^{-1}
1	**6**	0	34	Insoluble	—
2	**11**	0	4	Insoluble	—
3	**16**	0	41	Insoluble	—
4	**7a**	0	18	Insoluble	—
5	**7b**	0	33	Insoluble	—
6	**12a**	0	47	Insoluble	—
7	**12b**	0	39	Insoluble	—
8	**17a**	0	41	Insoluble	—
9	**17b**	0	39	Insoluble	—
10	**7a**	20	21	Soluble in $CHCl_3$, MeOH, EtOH, DMF, H_2O	0.12
11	**7b**	20	26	Soluble in the same solv. as those for No. 10 and acetone	0.18
12	**12a**	20	17	Soluble in the same solv. as those for No. 10	0.15
13	**12b**	20	31	Soluble in the same solv. as those for No. 11	0.16
14	**17a**	20	18	Soluble in the same solv. as those for No. 10	0.16
15	**17b**	20	33	Soluble in the same solv. as those for No. 11	0.16

a) 20 wt% total monomers in DMF; 3% AIBN/monomers; 50 °C, 72 h. b) Intrinsic viscosity in DMF at 25 °C.

leaving the reactive 2-position intact for further electophilic reactions.

Experimental

p- and *m*-Vinylanilines were synthesized according to the methods of Kamogawa[3] and Manecke,[4] respectively. 1-(Phenylsulfonyl)pyrrole (**2**), 3-acetyl-1-(phenylsulfonyl)pyrrole (**3**), methyl 1-(phenylsulfonyl)-3-pyrrolylacetate (**8**), 3-pyrrolylacetic acid (**10**), and 4-[1-(phenylsulfonyl)-3-pyrroly]butyric acid (**14**), were also synthesized following known methods.[5,6]

1-Phenylsulfonyl-3-pyrrolecarboxylic Acid (4). The haloform reaction was applied to **3**. Thus, to an alkaline solution of bromine (4.7 g) in H_2O–dioxane (1:1, 40 ml) cooled with ice was added a solution of **3** (3.0 g, 12 mmol) in dioxane (5 ml), followed by stirring for 5 h. The reaction mixture was diluted with cold water and extracted with ether. The aqueous layer was acidified with 6M H_2SO_4 and extracted with ether(1 M=1 mol dm^{-3}), followed by working-up to afford crystalline powder of mp 146—148 °C in 68% yield. IR (KBr) 3420 cm^{-1}. NMR ($CDCl_3$–DMSO-d_6) δ=9.0 (B, 1H).

***p*-Vinylbenzyl 3-Pyrrolecarboxylate (6).** *p*-Vinylbenzyl chloride (3.1 g, 20 mmol) was added to a solution of **5** (1.1 g, 10 mmol), prepared by alkaline hydrolysis of **4**, and triethylamine (TEA; 1.5 g, 15 mmol) in DMF (10 ml) and the mixture was stirred at 20 °C for 24 h with exclusion of moisture. The reaction mixture was poured into water and extracted with ether (150 ml). The organic layer was washed first with 5% aq Na_2CO_3, then with water, and worked up. Silica-gel (WAKOGEL C-300) column chromatography gave fluid in 45% yield. IR ($CHCl_3$) 3450, 1710, 990, 900 cm^{-1}. NMR ($CDCl_3$) δ=5.3 (s, 2H), 5.6 (q, 2H), 6.9 (q, 1H), 6.3—8.0 (m, 8H).

***N*-(*p*-Vinylphenyl)-3-pyrrolecarboxamide (7a).** Methyl chloroformate (0.9 g, 10 mmol) was gently added to a solution of **5** (1.1 g, 10 mmol) and TEA (1.4 ml, 10 mmol) in anhyd. THF (20 ml) at −15—−5 °C with vigorous shaking. Upon stirring for 10 min, a solution of *p*-vinylaniline (1.2 g, 10 mmol) and TEA (1.4 ml, 10 mmol) in $CHCl_3$ (20 ml) was further added below 0 °C with shaking, followed by stirring at this temperature for one hour and subsequent stirring at 20 °C for 24 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was worked up and recrystallization from benzene–hexane provided crystalline powder of mp 64—66 °C in 33% yield. Found: C, 73.26; H, 5.60; N, 13.11%. Calcd for $C_{13}H_{12}N_2O$: C, 73.58; H, 5.66; N, 13.21%. IR (KBr) 3440, 1680, 990, 900 cm^{-1}. NMR (DMSO-d_6–$CDCl_3$) δ=5.4 (q, 2H), 6.7 (q, 1H), 6.5—8.0 (m, 8H), 9.5 (s, 1H). MS *m/z* 212 (M$^+$).

***N*-(*m*-Vinylphenyl)-3-pyrrolecarboxamide (7b).** The same procedure as that for **7a** provided viscous mass in 19% yield. Found: C, 73.66; H, 5.50; N, 13.09%. MS *m/z* 212 (M$^+$).

***p*-Vinylbenzyl 3-Pyrrolylacetate (11).** The same procedure as that for **6** was applied to afford fluid in 53% yield. IR ($CHCl_3$) 3480, 1730, 990, 900 cm^{-1}. NMR ($CDCl_3$) δ=3.5 (s, 2H), 5.1 (s, 2H), 5.5 (q, 2H), 6.6 (q, 1H), 6.6—9.0 (m, 8H).

***N*-(*p*-Vinylphenyl)-3-pyrrolylacetamide (12a).** The same procedure as that for **7a** provided crystalline powder of mp 86—87 °C in 66% yield. Found: C, 74.32; H, 6.20; N, 12.17%. Calcd for $C_{14}H_{14}N_2O$: C, 74.34; H, 6.19; N, 12.39%. IR (KBr) 1650, 990, 900 cm^{-1}. NMR ($CDCl_3$—SO-d_6) δ=3.5 (s, 2H), 5.4 (q, 2H), 6.5 (d, 3H), 6.7 (q, 1H), 7.0—7.8 (m), 9.6 (s, 1H), 10.4 (b, 1H). MS *m/z* 226 (M$^+$).

***N*-(*m*-Vinylphenyl)-3-pyrrolylacetamide (12b).** The same procedure as that for **7b** afforded viscous mass in 21% yield. Found: C, 74.62; H, 6.29; N, 12.01%. MS *m/z* 226 (M$^+$).

4-(3-Pyrrolyl)butyric Acid (15). Prepared in the same manner as that for **10**. Care was taken so as to keep the pH value of the solution at 2—3 in the isolation of the free acid **15**. Crystalline powder of mp 89—91 °C in 31% yield. Found: C, 62.37; H, 7.52; N, 9.52%. Calcd for $C_8H_{11}NO_2$: C, 62.75; H, 7.19; N, 9.15%. IR (KBr) 3400, 1700 cm^{-1}. NMR (DMSO-d_6–$CDCl_3$) δ=1.0—2.8 (m, 6H), 5.5—6.8 (d, 3H), 9.0—10.6 (b, 2H).MS *m/z* 153(M$^+$).

***p*-Vinylbenzyl 4-(3-Pyrrolyl)butyrate (16).** The same procedure as that for **6** provided viscous mass in 34% yield. IR ($CHCl_3$) 3480, 1730, 990, 900 cm^{-1}. NMR ($CDCl_3$) δ=1.0—2.8 (m, 6H), 5.1 (s, 2H), 5.5 (q, 2H), 6.7 (q, 1H), 5.8—8.0 (m, 8H).

***N*-(*p*-Vinylphenyl)-4-(3-pyrrolyl)butyramide (17a).** The same procedure as that for **7a** afforded crystalline powder of mp 71—72 °C in 59% yield. Found: C, 75.40; H, 7.02; N,

11.05%. Calcd for $C_{16}H_{18}N_2O$: C, 75.59; H, 7.09; N, 11.02%. IR (KBr) 1650, 990, 900 cm^{-1}. NMR (DMSO-d_6–$CDCl_3$) δ=1.4—3.6 (m, 6H), 5.4 (q, 2H), 6.7 (q, 1H), 5.8—7.7 (m, 7H), 9.8—10.7 c(b, 2H). MS m/z 254 (M^+).

***N*-(*m*-Vinylphenyl)-4-(3-pyrrolyl)butyramide (17b).** The same procedure as that for **7b** provided viscous mass in 16% yield. Found: C, 75.62; H, 7.28; N, 11.11%. MS m/z 254 (M^+). IR and NMR for **7b**, **12b**, and **17b** were essentially the same as those for **7a**, **12a**, and **17a**, respectively.

Polymerization of Pyrrole Monomers. In a typical example, a pyrrole monomer, with or without addition of comonomer, 1-vinyl-2-pyrrolidone (VP), and α,α'-azobisisobutyronitrile (AIBN; 3%/monomer) were dissolved in *N*,*N*-dimethylformamide (DMF; 3 ml) so as to afford 20 wt% monomer concentration. The solution was put into a glass ampule, which was then sealed under N_2 in a conventional manner. The sealed tube was kept at 50 °C for 72 h and the content was poured into ether to precipitate the polymerization product. IR (KBr) 1650 cm^{-1}.

References

1) P. G. Sammes, "Comprehensive Organic Chemistry," Pergamon Press, Oxford (1979), Vol. 4, p. 275.
2) R. H. Yocum and E. B. Nyquist, "Functional Monomers II," Marcel Dekker, New York (1974), p. 142.
3) H. Kamogawa, *J. Polym. Sci., Part A-1*, **7**, 725 (1969).
4) G. Manecke and G. Rossmehl, *Markomol. Chem.*, **70**, 112 (1964).
5) J. Rokach, P. Hamel, M. Kakushima, and G. M. Smith, *Tetrahedron Lett.*, **22**, 4901 (1981).
6) M. Kakushima, P. Hamel, R. Frenette, and J. Rokach, *J. Org. Chem.*, **48**, 3214 (1983).