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# Synthesis of Polymers Containing Free Radical Verdazyl

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NOTE

# Synthesis of Polymers Containing Free Radical Verdazyl

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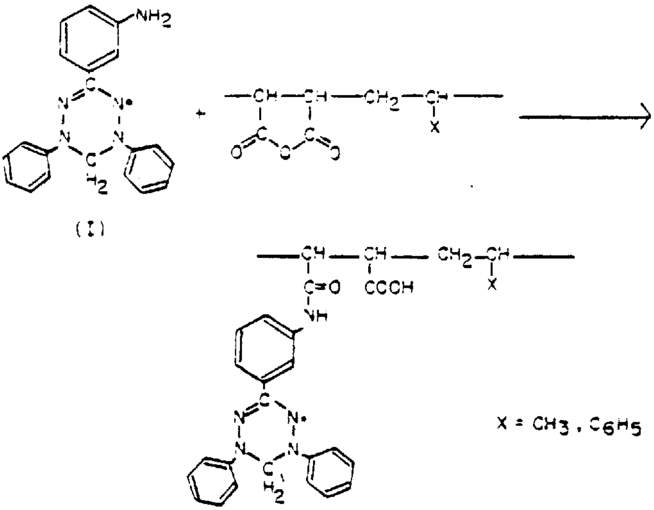
In preceding papers the authors have reported on the syntheses of polymers containing a new type of free radical verdazyl [1, 2] through the anionic polymerization of vinyl verdazyl monomers [3, 4]. In this paper we wish to report on the synthesis of polymer verdazyl by the reaction of verdazyl having amino group I with copolymers of maleic anhydride.

1,5-Diphenyl-3-(3'-aminophenyl)-verdazyl (I) was prepared through the catalytic hydrogenation of 1,5-diphenyl-3-(3'-nitrophenyl)-verdazyl with Pd/$BaSO_4$ and subsequent air oxidation. (I) was reacted with styrene-maleic anhydride (1:1) copolymer or propylene-maleic anhydride (1:1) copolymer in anhydrous tetrahydrofuran (THF). The reaction mixture was poured into absolute ether to precipitate polymer verdazyl as a dark green powder. The results of the reaction are shown in Table 1.

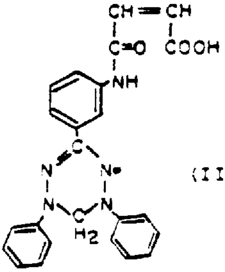
The contents of verdazyl group were determined by 1) the N content of the copolymers obtained, and 2) comparison of the absorption intensities of the copolymers with that of a reference compound II at 720 mμ. The copolymers showed no absorption corresponding to the verdazylium cation species (550 mμ).



(I)

X = $CH_3$, $C_6H_5$

IR spectra (KBr) of the copolymers showed the absorptions of carboxylic carbonyl (1700 cm$^{-1}$) and of amide carbonyl (1650 cm$^{-1}$). Figure 1 shows the ESR spectra of the copolymers and Compound II.



(II)

## EXPERIMENTAL

### Materials

### 1,5-Diphenyl-3-(3'-nitrophenyl)-verdazyl

A solution of 1,5-diphenyl-3-(3'-nitrophenyl)-formazan (20 g), methyl iodide (160 ml), $Ba(OH)_2.8H_2O$ (3.2 g), and BaO (80 g) in

TABLE 1. Results of the Reaction of Compound I with Maleic Anhydride Copolymers

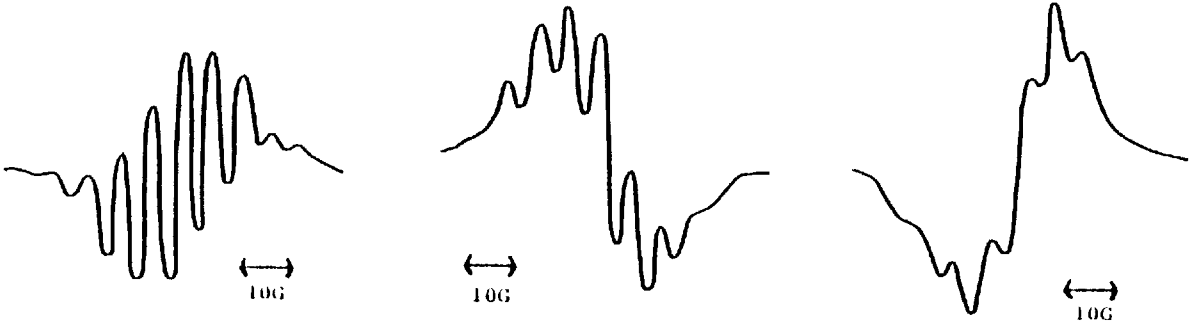
| Run | Polymer[a] (g) | Verdazyl (g) | Temp[b] (°C) | Time (min) | Yield (g) | Verdazyl content (mole %)[c] | Verdazyl content (N, %) | Verdazyl content (mole %)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | St-MAn 0.05 | 0.20 | 66 | 40 | 0.070 | 36 | (6.27) | 16 |
| 2 | St-MAn 0.05 | 0.20 | 66 | 120 | 0.090 | 47 | (9.16) | 22 |
| 3 | Pr-MAn 0.05 | 0.20 | 66 | 40 | 0.125 | 58 | (12.3) | 28 |

[a] St, Pr, and MAn indicate styrene, propylene and maleic anhydride, respectively.

[b] Refluxed in 8 ml of anhydrous THF.

[c] Determined by N analysis, mole % based on initial anhydride group.

[d] Determined by absorbance at 720 mμ in DMF with the reference compound II.



Compound (II) Copolymer Run 2 Copolymer Run 3

FIG. 1. ESR spectra of the copolymers and II in DMF.

N,N-dimethylformamide (DMF) (200 ml) was stirred for 6 hr at room temperature. The reaction mixture was filtered and diluted with benzene. The benzene solution was washed with water and dried over anhydrous sodium sulfate. Evaporation of benzene and recrystallization of the residue from methanol-DMF mixture gave dark green crystals: mp, 157-158°C; yield, 6.0 g (29%).

Analysis: Calculated for $C_{20}H_{15}N_5O_2$ (358.4): C, 67.03; H, 4.50; N, 19.54. Found: C, 66.83; H, 4.47; N, 19.41.

### 1,5-Diphenyl-3-(3'-aminophenyl)-verdazyl (I)

To a solution of 1,5-diphenyl-3-(3'-nitrophenyl)-verdazyl (2.0 g) in benzene (200 ml) was added Pd(5%) $BaSO_4$ (4 g), and hydrogen was passed through the solution. The solution changed from dark green to light brown and finally became clear. Inorganic compounds were removed, and the solution was left overnight at room temperature. Evaporation of benzene and recrystallization of the residue from methanol gave dark green crystals; mp, 122-123°C; yield, 1.3 g (72%); $\lambda_{max}^{benzene}$ 720 mμ (log ε = 3.547).

Analysis: Calculated for $C_{20}H_{18}N_5$ (328.4): C, 73.15; H, 5.52; N, 21.33. Found: C, 72.84; H, 5.59; N, 21.22.

### Reference Compound II

A solution of Compound I (250 mg) and maleic anhydride (75 mg) in THF-ether (1:2, 30 ml) was stirred for 1 hr at room temperature. The crystals deposited were separated and washed well with ether. Green crystals: mp, 148-150°C (decomp); yield, 0.17 g (53%); $\lambda_{max}^{benzene}$ 720 mμ (log ε = 3.537).

Analysis: Calculated for $C_{24}H_{20}N_5O_3$ (426.4): C, 67.59; H, 4.73; N, 16.42. Found: C, 67.40; H, 4.88; N, 15.87.

Another reference compound from Compound I and succinic anhydride could not be crystallized.

### Styrene- and Propylene-Maleic Anhydride Copolymer

Copolymerization was carried out in benzene at 50°C using benzoyl peroxide as an initiator. Compositions of the copolymers were determined by C analysis.

## Reaction of Compound I with Maleic Anhydride Copolymers

Copolymer (50 mg) was dissolved in anhydrous THF (8 ml) under reflux, then Compound I was added to the solution and the green solution was refluxed for a definite time. The reaction mixture was poured into ether to precipitate green polymer.

## Absorption Spectra

UV and ESR spectra were recorded in DMF solution at room temperature using a Hitachi EPS-3 Spectrometer and a JES-ME-3X Spectrometer equipped with 100 kHz field modulation.

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