

SYNTHESIS OF POLYSTYRENE CONTAINING VERDAZYL STRUCTURE

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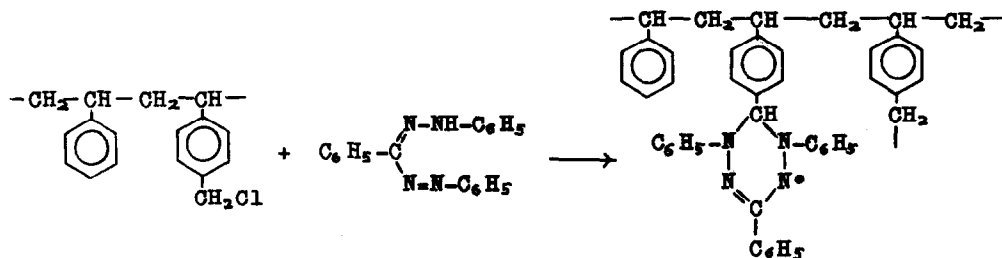
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Recently, the syntheses of polymeric free radicals bearing triphenyl methyl or diphenyl picryl hydrazyl structure were reported.¹⁾ However, the verdazyl, known as an extraordinarily stable free radical²⁾, has never been incorporated in macromolecule hitherto. We wish to describe here the synthesis and some reactions of polystyrene(PS) which has verdazyl structure in its matrix. Such a stable polymer radical is a special example of the "redox polymer" and may be expected to be a polymeric semiconductor and a polymeric catalyst for some oxidation-reduction reactions.

For example, to a cooled solution of 1,3,5-triphenyl formazan (1.35 g : 4.5 m mol), barium oxide (9.5 g) and barium hydroxide octahydrate (0.6 g) in dimethylformamide (DMF) (40 ml.), was added dropwise a solution of chloromethylated PS (1.0 g : 4.5 meq. Cl) in DMF (25 ml). After stirring for 30 hr. under air stream, green precipitate was collected. Treated with 2N-hydrochloric acid to remove barium salts, the color of polymer turned to violet. The color returned to green, however, by dispersing it in DMF for 3 hr. Polymer thus obtained was a green powder and insoluble in ordinary solvents presumably due to partially cross-linked network structure I. It contained no chlorine and the verdazyl content was 7.1 % (unit mole) based on nitrogen analysis. Corresponding model compound, 1,3,5,6,-tetraphenyl verdazyl II (m.p. 182-3°C) was also prepared by the reaction of benzyl chloride and 1,3,5-triphenyl formazan.

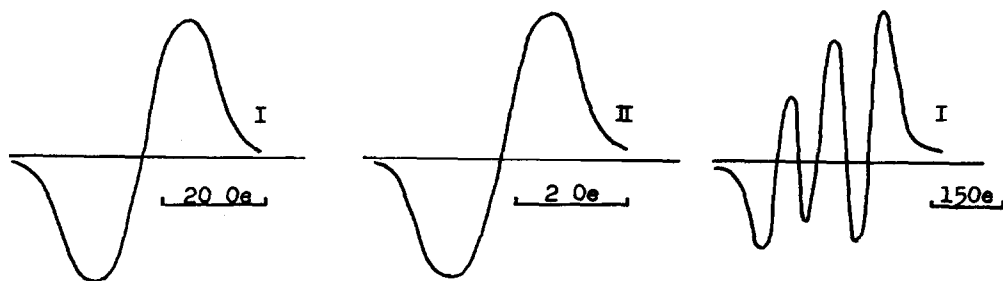


The e.s.r. spectra of I in solid state and in benzene solution were shown in FIG.1 together with that of model compound II. Fine structure, triplet, observed for I in solution indicated an unpaired electron located on N atom.

Fig.1

g=2.0035 (I)

g=2.0031 (II)

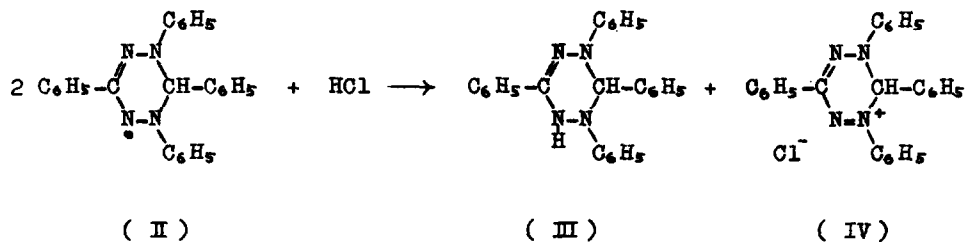


in solid state

in benzene

(saturated)

Potentiometric titration of II with hydrochloric acid indicated the purity was 96.7 % assuming the reaction proceeded as follows.



By the same procedure, verdazyl content in I was 4.1 % (unit mole). The IR absorption bands of I at 1600 ($\nu_{C=N}$) and 1480, 1370 cm^{-1} ($\nu_{C=C}$) agreed with those of model compound, II.

Absorption bands at 1660 ($\nu_{N=N^+}$) and 3350 cm^{-1} (ν_{N-H}) were characteristic of polymer I and indicated the presence of disproportionated structure III and IV remained unchanged by DMF treating. This also consisted with the difference in verdazyl content determined by nitrogen analysis and acid titration. The IR and e.s.r. spectra of green polymer (I) reported here were well consisted with those of model compound (II) and those of verdazyls reported by Kuhn²⁾. These results, together with some chemical stabilities and reactivities of (I) and (II) describe below, indicated the verdazyl structure was introduced into polystyrene matrix, even if partially.

I reacted with neither oxygen nor nitroxide radical of 2,2,6,6-tetramethyl-4-piperidone under mild condition. Both I and II turned color to violet at room temperature with such oxidizing agents as hydrogen peroxide, tert-butyl hydroperoxide, ferric chloride and cupric sulfate but no change was observed with potassium ferricyanide, potassium iodate, potassium periodate, p-benzoquinone, naphthoquinone and azoxybenzene. Both I and II became colorless with reducing agents such as sodium dithionite, stannous chloride and ascorbic acid but remained unchanged with sodium thiosulfate, hydroquinone and benzoin.

From these results, it may be concluded that the standard redox potential of I and II lie between + 0.45V (Cu^{2+}) and + 0.39V (ascorbic acid). Syntheses of another type of verdazyl polymers and characterization of polymeric radicals are in progress.

REFERENCES

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D.Braun and R.J.Faust. Angew.Chem., **78**, 905 (1966).
- 2) R.Kuhn and H.Trischmann, Monatsh.Chem., **95**, 457 (1964) and so on.