Asian Journal of Chemistry Vol. 9, No. 4 (1997), 589–591

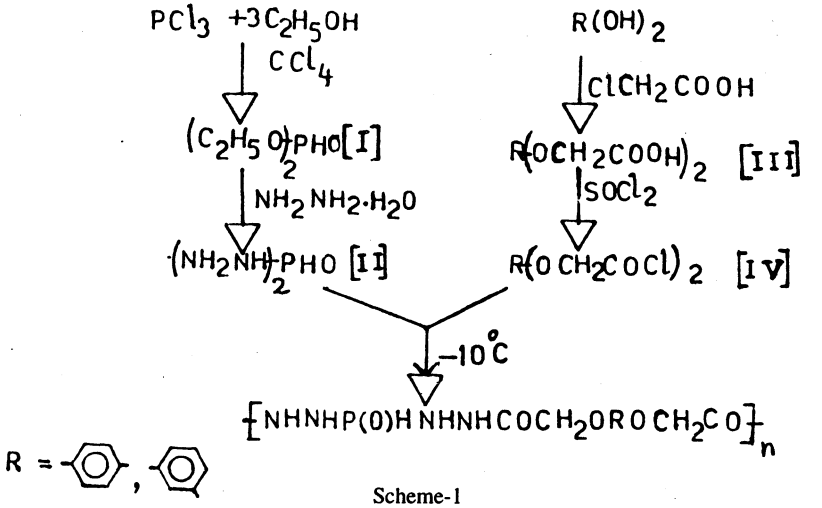
Synthesis and Characterization of Novel Polyetherhydrazides

J.S. SHUKLA† and MOHD. G.H. ZAIDI*
Department of Chemistry
Dr A.H. Rizvi Shia Degree College, Jaunpur-222 001, India

Novel polyetherhydrazides (PEHs) have been synthesized by suspension polycondensation of resorcin/hydroquin-O,O-bis(acetyl chlorides) and phosphonic dihydrazide in N,N-dimethyl acetamide at –10°C. All such PEHs have been characterized by IR spectral analysis, inherent viscosity, elemental analysis and oxidative isothermal weight loss analysis respectively.

INTRODUCTION

The mechanical and heart resistant properties of polyhydrazides can be enhanced by incorporation of aromatic rings in their backbone chain.[1] The introduction of ether bridge in their backbone may often improve the solution processability of various polyamides and polyhydrazides.[2] The degree of improvement is much enhanced when methylene groups are incorporated along with ether linkage in their backbone chain.[3] The present article deals with the synthesis and characterization of polyetherhydrazides from resorcin/hydroquin-O,O-bis(acetyl chloride) and phosphonic dihydrazide monomers. A typical reaction is shown in Scheme-1.



Scheme-1

†Department of Chemistry, Lucknow University, Lucknow-226 007, India.

EXPERIMENTAL

All chemicals and solvents employed for the synthesis of PEHs were of LR grade.

Diethylhydrogen phosphite (I) was synthesized according to the procedure discribed earlier.[4] b.p. 73–76°C/14 mm; yield 92%. $C_4H_{11}O_3P$ requires: C, 33.8; H, 7.8%; found: C, 35.0; H, 7.9%.

Phosphonic dihydrazide (II) was synthesized by known method.[5] m.p. 92°C. Yield 81.6%. N_4H_7OP requires: H, 6.36; N, 50.09%; found: H, 6.32; N, 50.90%. IR: 1500–1480 cm^{-1} δ(NH), 1300 cm^{-1} ν(PO) and 960 cm^{-1} δ(PH).

Resorcin/hydroquin-O,O-bis(acetic acids) have been synthesized by dissolving appropriate phenol (0.1 mole) in required quantity of sodium hydroxide solution (4.0 N). To this was added the solution of chloroacetic acid (0.6 mole) in water (250 mL). The solution was refluxed for 12–14 h. During this period it was kept alkaline by adding sodium hydroxide solution (200 mL, 4.0 N). The solution was cooled and neutralized by conc. HCl, dicarboxylic acids precipitated were filtered and crystallized by glacial acetic acid.

Hydroquin-O,O-bis(acetic acid): m.p. 250°C; yield 80.5%. $C_{10}H_{10}O_6$ requires: C, 53.09; H, 4.42%; found C, 53.12; H, 4.40%. resorcin-O,O-bis(acetic acid): m.p. 192°C; yield 70%. $C_{10}H_{10}O_6$ requires: C, 53.09; H, 4.42%, found: C, 53.00; H, 4.49%.

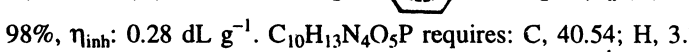
Resorcin/hydroquin-O,O-bis(acetylchlorides) were prepared by the procedure described earlier.[6]

N,N-Dimethylacetamide (DMAc) was dried over barium oxide for 48 h, followed by 2 h refluxing; b.p. 58–60°C/10 mm.

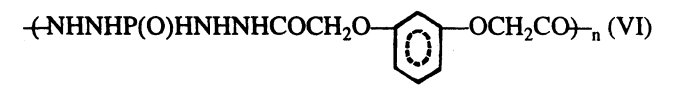
To suspension of phosphonic dihydrazide (0.01 mole) in N,N-dimethylacetamide (10 mL) was added appropriate diacid chloride (0.02 mole) in N,N-dimethylacetamide (20 mL) at –10°C with constant stirring up to 4.5 h. The inherent viscosity-time dependence relationships during the course of polycondensation have also been studied. All such polymers were precipitated by water and dried below 50°C.

RESULTS AND DISCUSSION

The inherent viscosities (η_{inh}) of all PEHs have been deduced at a concentration of 0.5 g dL^{-1} in *m*-cresol solution at 25 ± 1°C. All such PEHs have been characterized by IR spectra and elemental analysis.



Yield: 98%, η_{inh}: 0.28 dL g^{-1}. $C_{10}H_{13}N_4O_5P$ requires: C, 40.54; H, 3.37; N, 18.91%; found: C, 40.26; H, 3.02; N, 18.00%. IR: 3200–3100 cm^{-1} ν(NH), 1640 cm^{-1} ν(CO), 1450 cm^{-1} δ(NH), 1240 cm^{-1} ν(PO), 1100 cm^{-1} (PH. def.). and 815 cm^{-1} δ(HPO).



Yield: 97%; η_{inh}: 0.19 dL g^{-1}; found: C, 40.40; H, 3.21; N, 18.20%. IR: 3000 cm^{-1} ν(NH), 1645 cm^{-1} ν(CO), 1450 cm^{-1} δ(NH), 1220 cm^{-1} ν(PO), 1010 cm^{-1} (PH def.) and 810 cm^{-1} δ(HPO).

The inherent viscosity-time dependence of PEHs during the course of polycondensation indicates that the PEH (V) erived from hydroquin-O,O-bis(acetylchloride) monomer was polymerized in 2.5 h, while that of resorcin-O, O-bis(acetylchloride) in 4.2 h. These observations clearly show that the PEH containing *p*-phenylene ring was polymerized more regularly and orderly than the corresponding *m*-isomer.[7] The greater value of η_{inh} of (V) than (VI) also indicate that the rate of polycondensation of monomer (III) was greater than (IV).

The thermal stabilities of all such PEHs have been studied by oxidative isothermal weight loss analysis, where 100% volatilization of (V) was recorded in 90, 80 and 70 min at 200, 300 and 400°C respectively, while in case of (VI) the same volatilization was observed in 60, 40 and 20 min.

From the above discussions, it was concluded that the polyetherhydrazides (PEHs) of appreciable thermo-oxidative stability and inherent viscosity can be synthesized by selecting appropriate combination of monomers.

REFERENCES

1. P.R. Divornic, *J. Appl. Polym. Sci,*. **28**, 2729 (1983).
2. M. Kapuscinska, E.M. Pears, H.F.M Chung, C.C. Ching and Q.X. Zhou, *J Appl. Polym. Sci..*, **22**, 3999 (1984).
3. K. Saotime, Japanese Patent, 68, 13066; *Chem. Abstr.*, **70**, 12588f (1969).
4. H. Mc Combie, B.C. Saunders and G.J. Stacey, *J. Chem. Soc.*, **1**, 380 (1945).
5. W. Strecker and H. Heuser, *Ber.*, **57B**, 1557 (1924).
6. M. Srinivasan, K.J. Scariah, V.N. Krishnamurthy and K.V.C. Rao, *J. Appl. Polym. Sci.*, **22**, 1744 (1984).
7. J. Preston and W.B. Black. *J. Polym. Sci. (C)*, **19**, 7 (1967).

(*Received*: 18 September 1996; *Accepted:* 15 May 1997) AJC-1257