Tetrahedron Letters,Vol.27,No.50,pp 6129-6132,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

ARENEDIAZONIUM TETRAFLUOROBORATES AS INITIATORS IN THE POLYMERISATION OF HALOARENETHIOLATES. A SIMPLE AND MILD ACCESS TO POLY(ARYLENE SULFIDE)S.

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Abstract: Polymerisation of *p*-bromobenzenethiolate to poly(*p*-phenylene sulfide) is unprecedentedly achieved in DMSO by the employment of catalytic amounts of a diazonium salt *via* a radical, radical-anion chain pathway. The synthesis is likewise applicable to methyl substituted poly(*p*-phenylene sulfide)s as well as to poly(*m*-phenylene sulfide).

In the field of heat-resistant polymers, poly(*p*-phenylene sulfide) (*p*-PPS) occupies a pre-eminence position[1] due to its mechanical properties, enhanced by curing at high temperature,[1] and to the possibility of both melt- and solution-processibility. Moreover, *p*-PPS has also recently stepped into the growing field of organic conductors, given the appreciable conductivity reached with a number of today well assessed chemical or electrochemical doping methods.[2]

The industrial synthesis of *p*-PPS generally exploites the nucleophilic replacement of halogen from *p*-dichlorobenzene. Patented systems employ either sodium sulfide in *N*-methyl pyrrolidone[3] at 250 °C or sulfur and dry sodium carbonate in the melt.[4] Besides these methods and the analogous self-condensation of *p*-halobenzenethiolates,[5] the exploitation of sulfur or sulfur derivatives in electrophilic or homolytic substitutions on arenes or haloarenes has recently been reported.[6] In all the systems above, though, rather drastic reaction conditions are required, and in some cases unreproducible branching and/or crosslinking in the polymeric material is observed.[5b]

Recently we have reported[7a] that the reaction between benzenediazonium tetrafluoroborate and *p*-chlorobenzenethiolate in DMSO, proceeding *via* an $S_{RN}1$ mechanism, leads, besides to the diaryl sulfide (**1** : n = 1) as the main product, to quantifiable amounts of (**1** : n = 2 or 3) (eq i).

(**1**)

(i)

Accordingly, we have examined the possibility that the system above represent an unprece-

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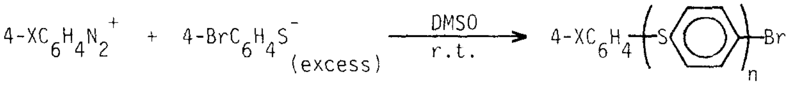
§ Part of M.L. Sartirana's thesis for the Research Doctoral Degree in Chemistry.

dented mild and simple access to p-PPS. The herewith reported preliminary experiments have been carried out by the addition, at room temperature, of a catalytic amount of solid arenediazonium tetrafluoroborate to a stirred DMSO solution of sodium p-bromobenzenethiolate (eq ii),



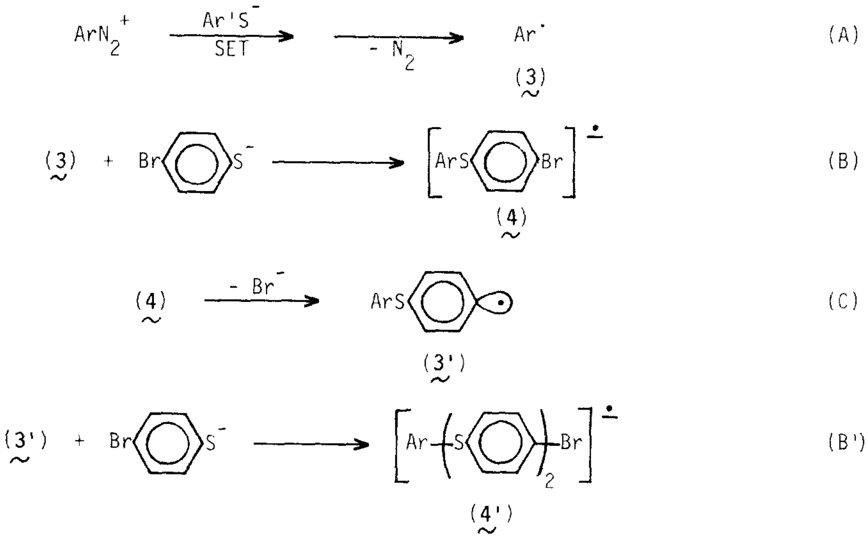
(ii)

X = H, Br

(2)

the reaction being kept under a positive pressure of argon for the time reported in the Table. The almost colourless insoluble material formed was filtered, washed carefully with methanol and successively with water, dried, and analysed as such or after continuous extraction with THF. Analyses and further experimental details are reported in the Table.

It should be first of all pointed out that IR spectra always showed good qualitative agreement with that of a commercial sample of p-PPS, suggesting, though, a higher degree of crystallinity with respect to the latter.[8] Furthermore, although the so far attained degree of polymerisation cannot compare with that reported for the commercial product,[2b] the data in the Table show an increase of the melting point (T_m) with n up to a plateau value for $n \geq 10$. Such a pattern suggests a strict linearity of the isolated polymers. This outcome, which should represent an advantage as to the technical properties of the material, fulfils our expectations[7] and can be well accounted for with the step sequence depicted below. Single-electron transfer



from the thiolate to the initiator (either the diazonium cation itself or a rapidly formed covalent diazosulfide[7a]) leads to the σ radical $Ar^{\cdot}$. Growth of the chain is henceforth guaranteed by the alternance of steps (B) (radical/anion coupling) and (C) (expulsion of bromide with generation of a new radical). Interruption of such alternance can be caused by a number

Table. *Poly(p-phenylene sulfide) from 0.6* M *4-*BrC_6H_4SNa *in the presence of catalytic amounts of a* diazonium tetrafluoroborate as initiator (in DMSO, at room temperature).

Expt	ArN_2^+	Thiolate/Diazonium molar ratio	Time (h)	Yield[a,b] (%)	T_m[b,c] (°C)	Br%[b]	n_{Br}[b,d]
1	$4\text{-}BrC_6H_4N_2^+$	30	24	18.0 (8.0)	241 (254)	16.5 (12.3)	6.8 (9.8)
2	"	150	24	5.6 (4.1)	258 (260)	13.2 (11.4)	9.0 (10.8)
3	"	from 150 to 50[e]	24	18.6 (14.7)	260 (264)	12.6 (10.5)	9.6 (11.9)
4	"	from 150 to 30[e]	24	24.9 (17.6)	255 (262)	13.2 (10.8)	9.0 (11.5)
5	"	from 150 to 19[e]	48	28.2 (13.7)	234 (254)	16.5 (12.8)	6.8 (9.4)
6	$C_6H_5N_2^+$	30	24	15.6 (5.1)	230 (244)	9.7 (8.6)	6.2 (7.1)
7	"	150	24	3.9 (2.2)	249 (252)	8.4 (8.0)	7.3 (7.8)

[a] Yield of precipitated material: by weight, with respect to the initial thiolate and taking into account loss of NaBr. [b] Figures in parentheses refer to the product recovered after continuous extraction (12 h) with THF. [c] Melting point, determined by thermal analysis with a differential scanning calorimeter. [d] See formula (**2**) in the text: calculated from the elemental analysis, under the assumption of bromine being present at both ends of the polymeric chain, except when employing the unsubstituted benzenediazonium salt as initiator. [e] Successive additions of initiator during reaction, generally at 2 h intervals.

of undesired events, such as oxidation of a radical anion by residual initiator or, more likely, radical/radical coupling or H-atom transfer to a radical from the medium. It must be pointed out that polymerisation of *p*-chlorobenzenethiolate *via* radical and radical-anion intermediates has been reported.[9] Anyway, while, on one side, systematic analysis with characterisation of products was not performed, on the other side the reaction was carried out under photostimulation, with or without the addition of a haloarene as initiator. Herein conditions are quite different as irradiation is not required and the reaction smoothly takes off upon mixing of the reactants. As a matter of fact, attempted photostimulation proved here to be ineffective, both qualitatively and quantitatively, although a faster formation of polymeric material on the irradiated vessel walls could be observed.

A few factors that influence the yield and/or the characteristics of the product (as judged by the calculated molecular weight and/or the melting point) can be evidenced. (*a*) The possibility for the chain to grow in both directions (as obtained when the initiator contains itself an additional suitable leaving group such as bromine) leads to a better product (cf expts 1 and 2 with expts 6 and 7 respectively). This suggests that the insolubilisation of the growing chain does not represent the only limiting factor as to the attainable degree of polymerisation. (*b*) At constant initial concentration of thiolate, an increase in the $Ar'S^-/ArN_2^+$ molar ratio is accompanied by a higher efficiency of the initiator with formation of longer chains (cf expts 1 and 2). Consequently, while the yield calculated with respect to the thiolate decreases, figures rise to somewhat higher values when allowing for the decreased amount of initiator employed. (c) Repeated additions of initiator during reaction lead to higher percentages of conversion but a limit is expectedly posed to such procedure as far as the quality of the recovered polymer is concerned (cf expts 2 to 5).

The applicability of the present polymerisation route to the synthesis of methyl substituted p-PPS's (from 4-Br-2-Me$C_6H_3S^-$, 4-Br-3-Me$C_6H_3S^-$, and 4-Br-2,6-$Me_2C_6H_2S^-$) as well as of m-PPS (from 3-Br$C_6H_4S^-$) has also been positively tested, indicating that the system herein provides a potential access to poly(arylene sulfide)s in general. Research is accordingly in progress in order to both widen its scope and optimise yields and degree of polymerisation as well as to investigate the technical applicability of the resulting polymers.

Aknowledgements: We are indebted to Prof. C. Dell'Erba and to Prof. E. Bianchi for helpful discussion.

References

1 - R.T.Hawkins, Macromolecules, 1976, 9, 189, and refs cited therein; D.O.Tieszen, U. S. Patent 3853824 (1974); J.P.Blackwell, U. S. Patent 3776880 (1973).

2 - (a) J.E.Frommer, Acc. Chem. Res., 1986, 19, 2; S.Tokito, T.Tsutsui, and S.Saido, Polym. J., 1985, 17, 959; D.Bloor, Chem. Brit., 1983, 725; J.F.Rabolt, T.C.Clarke, K.K.Kanazawa, J.R. Reynolds, and G.B.Street, J. Chem. Soc., Chem. Commun., 1980, 347; (b) L.W.Shacklette, R.L. Elsenbaumer, R.R.Chance, H.Eckhardt, J.E.Frommer, and R.H.Baughman, J. Chem. Phys., 1981, 75, 1919, and refs cited therein.

3 - J.T.Edmonds and H.W.Hill, U. S. Patent 3354129 (1967).

4 - A.D.Macallum, J. Org. Chem., 1948, 13, 154; U. S. Patents 2513188 (1950) and 2538941 (1951).

5 - (a) S.Tsunawaki and C.C.Price, J. Polym. Sci., Part A, 1964, 2, 1511; (b) R.W.Lenz, C.E. Handlovits, and H.A.Smith, J. Polym. Sci., 1962, 58, 351.

6 - J.Laakso, B.Hortling, K.Levon, and J.J.Lindberg, Polym. Bull., 1985, 14, 225, and refs cited therein.

7 - (a) G.Petrillo, M.Novi, G.Garbarino, and C.Dell'Erba, Tetrahedron, 1986, 42, 4007; (b) Tetrahedron Lett., 1985, 26, 6365.

8 - T.C.Clarke, K.K.Kanazawa, V.Y.Lee, J.F.Rabolt, J.R.Reynolds, and G.B.Street, J. Polym. Sci., Polym. Phys. Ed., 1982, 20, 117; D.G.Brady, J. Appl. Polym. Sci., 1976, 20, 2541.

9 - R.A.Alonso and R.A.Rossi, J. Org. Chem., 1980, 45, 4760; see also W.R.Bowman, H.Heaney, and P.H.G.Smith, Tetrahedron Lett., 1984, 25, 5821.

(Received in UK 6 October 1986)