Polymer Bulletin 23, 295–298 (1990)

Polymer Bulletin

Effect of the polymer structure and tacticity on the oxidizing ability of polyvinylpyridinium dichromate

B. Tamami* and N. Goudarzian

Department of Chemistry, Shiraz University, Shiraz, Iran

Summary

Poly(2-vinylpyridinium dichromate) oxidizes different alcohols to their corresponding carbonyl compounds more efficiently than poly(4-vinylpyridinium dichromate). Syndiotactic form of the 2-isomer is the most efficient.

Introduction

Differences in the behavior and properties between some derivatives of poly(4-vinylpyridine) and poly(2-vinylpyridine) have been reported in the literature. Only the 2-isomer can be made with different tacticities which show also interesting physical and chemical behavior (1-6).

Except for a few cases almost all of the polymeric reagents based on polyvinylpyridines have been prepared from poly(4-vinylpyridine) (8,9). Recently in the course of our investigation on preparation and uses of some new polymeric oxidizing reagents, using polyvinylpyridines and their N-oxides as supports, we have come across the fact that the supported reagents made from poly(2-vinylpyridine) are considerably more effective than those made from the 4-isomer (10). Polyvinylpyridine supported silver dichromate was such a reagent which the supported 2-isomer was more reactive (11).

We now wish to report the effect of the polymer structure and also tacticity on the oxidizing ability of polyvinylpyridinium dichromate, a polymeric reagent which has long been made and commercialized for the oxidation of hydroxy organic compounds (12,13).

Results and Discussion

Poly(4-vinylpyridinium dichromate)(AP4) and poly(2-vinylpyridinium dichromate)(AP2) were made from the corresponding atactic polymers having close molecular weights. The capacities in terms of m.mol. $Cr_2O_7^{=}$ per gram of the reagents were almost identical for these two polymeric reagents. Oxidation of different hydroxy compounds with (AP2) showed that

---

*To whom offprint requests should be sent this reagent was considerably more efficient than (AP4). Changing the solvent had no effect on this difference in efficiency.

Furthermore, mainly isotactic and mainly syndiotactic poly(2-vinylpyridines) were prepared according to the known procedure (5-7) and the dichromate anions were fixed onto them. Investigation on these reagents revealed that the tacticity of the polymer can effect its efficiencies in the oxidation of different hydroxy organic compounds. Under similar conditions syndiotactic form (SP2) proved to be more efficient than the isotactic form (IP2).

As shown in table (I), comparing (AP2) with (AP4), the former oxidizes the alcohols to their corresponding carbonyl compounds in almost half the time spent by the latter. It is also observed that (SP2) is almost twice as efficient as (IP2) in the same oxidation reactions, and with (AP2) somewhere in between. It is interesting to notice that the syndiotactic form (SP2) is the most efficient among different polyvinylpyridinium dichromates, and with respect to the 4-isomer by a factor of 3-4 times.

Considering the facts that the capacities of these polymeric reagents were almost identical, the molecular weights of the polymer supports were close, and that the same sort of behavior was observed in different solvents, we have come to the conclusion that such differences are mainly due to the differences in structure and tacticity of the polymers.

Fixation of $Cr_2O_7^=$ anions onto poly(2-vinylpyridine) is probably different compared to poly(4-vinylpyridine). In the former polymer the N atoms of the rings are close to the main chain compared to the latter polymer in which they are exposed and far away from the main chain. In addition the 2-isomer probably has a more compact structure due to slight interactions between the H's of the chain and the nitrogens of the rings (2,6). Models (Courtauld) of the isotactic poly-(2-vinylpyridine) having the spiral conformation (5) and syndiotactic form having a polymer zigzag conformation (2), show that the nitrogens of adjacent rings are positioned differently in space in these too stereoregular polymers.

Considering the above assumptions one can suggest that the higher efficiencies of (AP2) with respect to (AP4) and (SP2) over (IP2) are probably due to the higher local concentration and / or better availibility of $Cr_2O_7^=$ groups on these polymer supports for reaction with the interacting substrates.

The same sort of behavior have also been observed for crosslinked poly(2-vinylpyridinium dichromate) and its 4-isomer which will be reported soon.

Table (I) Oxidation of Alcohols to their Corresponding Carbonyl Compounds with Polyvinylpyridinium Dichromate.

-No	$-CH_2OH$	Reagent[a,b,c]	Time (min)	%Yield
1	Benzyl alcohol	AP4	80	80-85
		AP2	50	95-100
		IP2	75	100
		SP2	30	100
2	Cinnamyl alcohol	AP4	210	80
		AP2	120	80
		IP2	150	80
		SP2	75	80-85
3	1-Phenylethanol	AP4	170	85
		AP2	65	80-85
		IP2	80	75-80
		SP2	40	80
4	Piperonyl alcohol	AP4	180	70-75
		AP2	75	80
		IP2	90	80
		SP2	50	85
5	Benzhydrol	AP4	110	90
		AP2	60	80-85
		IP2	80	80-85
		SP2	30	90
6	2-phenylethanol	AP4	230	80
		AP2	125	75-80
		IP2	145	75-80
		SP2	75	75-80
7	Benzoin	AP4	240	80
		AP2	180	80-85
		IP2	230	75
		SP2	120	80-85

a. A: Atactic; I: Mainly Isotactic; S: Mainly Syndiotactic; P4: Poly(4-vinylpyridinium dichromate); P2: Poly(2-isomer).

b. Intrinsic viscosities of the original polymer supports in ethanol-water (92/8wt) at 25°C: AP4 (0.43); AP2(0.48); IP2(0.47); SP2(0.42).

c. Capacities, m.mol of $Cr_2O_7^{=}$ per gram of reagent: AP4(2.13); AP2(2.16); IP2(2.15); SP2(2.12).

Experimental

Polyvinylpyridines were prepared by suspension polymerization of the corresponding monomers. Isotactic and syndiotactic poly(2-vinylpyridines) were prepared according to the reported procedures (5,6). Polymer samples of close molecular weights in the range of 7.2-88x10^4 , as determined by their intrinsic viscosities (14), were used. Fixation of the dichromate anions onto the polymers were done by the usual procedure (12), with some modification due to the solubility behavior of the polymers. Capacities were determined by titration and / or atomic absorption technique.

General procedure for the oxidation of alcohols: To a solution of alcohol (2 mmol) in toluene (20 ml) in a 50 ml round bottomed flask equiped with a condenser and a magnetic stirrer, polymeric reagent (1g, wetted)(12) was added and refluxed for (30 min-4 hr). Progress of the reaction was monitored by t.l.c. (eluent: hexane-ether). The reaction mixture was cooled to room temperature and filtered, accompained by repeated washings. The desired carbonyl compound was purified on a silica gel column with appropriate eluent. The results are shown in table (I).

Aknowledgement

We are grateful to Shiraz University Research Council for the partial support of this work.

References and footnotes

1. Holt P.F, Nassrallah E.T (1986) J. Chem. Soc. B: 233
2. Holt P.F, Lindsay H (1969) J. Chem. Soc. B: 54
3. Holt P.F, Tamami B (1970) Polymer: 553
4. Holt P.F, Lindsay H, Beck E.G (1970) Br. J. Pharma. 38: 192
5. Natta G, Mozzanti G, Longi P, Dall asta G, Bernardini F (1961) J. Polym. Sci. 51: 486, and (1960) Makromol. Chem. 37: 160
6. Geuskens G, Lubikulu J.C, David C (1966) Polymer 7: 63
7. Information about the tacticities of the Polymers were obtained by using high resolution nuclear magnetic resonance spectroscopy, a method reported in ref. 6.
8. Akalah A, Sherington D.C (1981) Chem. Rev. 81: 557
9. Frechet J.M.J, Meftahi M.Y (1984) Brit. Polym. J. 16: 164
10. Unpublished results.
11. Tamami B, Hatam M, Mohadjer D (1989) Polymer Bull. 21: 531
12. Frechet J.M.J, Darling P, Faral M.J (1981) J. Org. Chem. 46: 1728
13. Aldrich Cat. No. 23746-9(1988).
14. Brandrup J, Immergut E.H (1966) Polymer Handbook, 2nd edn. John Wieley, New York.

Accepted January 4, 1990 S