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PVC modification with bifunctional thiol compounds

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Summary

The chemical modification of PVC with bifunctional thiol compounds is reported. Aliphatic as well as aromatic compounds were tested under different reaction conditions. The modified PVC's were studied by IR and H-NMR.

Introduction

PVC is one of the most important commercial polymers. However, the purpose of materials based upon PVC is limited due to its inferior thermal and mechanical properties. A way to minimize these shortcomings is to increase the intermolecular force by introducing hydrophilic groups into PVC chains. The introduction of hydrophilic groups would also increase the polarity and change solubility characteristics of PVC and thus open the way to new applications.

One possibility to achieve this aim is to make use of the nucleophilic substitution reaction. It is well known (1) that thiol compounds can be used for this purpose due to the high nucleophilicity and low basicity of the sulfur.

In previous work we have studied the substitution reaction of PVC with different reagents, especially monofunctional thioderivates in solution and in the melt, either in discontinuous or continuous medium, with two purposes. One was the study of substitution mechanism of the polymer (2-4) and the other to improve polymer properties with the aid of tailor made reagents (5-8). Nevertheless, to find new applications to this polymer, i.e. for membrane uses, other reactants of bifunctional nature needed to be tested. There have been reported several reactions of PVC with difunctional reagents (9-12) in which it was not possible to separate substituted from crosslinked products.

In this paper we describe the modification of PVC with a series of commercial and non-commercial products containing a thiol group and a further functional group. Reaction parameters like temperature, solvent and base were varied to find the optimal conditions.

Experimental

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were M_W= 112000 g/mol and M_N= 48000. The tacticity measured by ^{13}C-NMR was syndio= 30.6%, hetero= 49.8% and iso= 19.6%. Cyclohexanone (C.H.) and Dimethylsulfoxide (DMSO) were dried by refluxing and distillation over Calcium hydride.

2,2'-Diethanoldisulfide **1** was synthesized by H_2O_2-oxidation of 2-mercaptoethanol in aqueous solution with ammonia as a catalyst.

The reaction mixture was maintained at 50°C. After 2hours a white crystalline product had formed which could be filtered off and dried. Melting point 25°C, Yield: 80%

The Dipyranylether of 2,2'-Diethanoldisulfide **2** was prepared by stirring equimolar amounts of **1** and 3,4-Dihydropyran in a diethylether solution for 4 hours at room temperature using p-Toluenesulfonic acid as a catalyst. The reaction mixture was washed with 10% $NaHCO_3$ and water and dried over $NaSO_4$. Then the ether was stripped off and the residue used for the next reaction without further purification. Yield: 85%

2-Mercaptoethylpyranylether **6** was obtained by reduction of **2** with $LiAlH_4$ in diethylether. The reaction mixture was refluxed for 1 hour. Then ice and 15% H_2SO_4 were added and the phases separated. The organic phase was washed with $NaHCO_3$ and water and dried over Na_2SO_4. Then the ether was stripped off and the residue distilled under reduced pressure (bp$^{0.5}$.:61). Yield: 80%

d ($CDCl_3$): 4.6 (s, CH), 3.95-3.75 (m, ring-CH_2O), 3.55-3.4 (m, CH_2O), 2.7 (q, CH_2S), 1.9-1.45 (m, ring-CH_2), 1.4 (t, SH).

2-Mercapto benzoic acid methyl ester **8** was prepared according to a standard esterification method from commercial 2-mercapto benzoic acid in HCl saturated methanol. The ester was distilled under reduced pressure (bp$^{0.5}$.: 85°C). Yield: 80%

d (DMSO-d6): 7.9 (d, aromatic H), 7.55 (d, aromatic H), 7.4 (t, aromatic H), 7.2 (t, aromatic H), 5.3 (s, SH).

The synthesis of 4-mercapto benzylalcohol **12** and 2-mercapto benzyl alcohol **13** is described elsewhere (7).

4-Nitrothiophenol ***10*** was purchased from Aldrich as a technical product with a purity degree of 80%. It was purified by means of flash chromatography on silica gel using a 1:1-mixture of hexane/ CH_2Cl_2 as the eluent. d ($CDCl_3$): 8.1 (d, aromatic H), 7.4 (d, aromatic H), 3.8 (s, SH).

All other compounds used for PVC modification reactions were commercial grade and used without further purificaion.

Salt formation of thiol compounds was realized by adding a 5%-molar excess of sodium hydride (60% dispersion in mineral oil, Aldrich) suspended in dry THF to a THF solution of the respective product at 0°C. The reaction mixture was filtered to eliminate unreacted NaH and then precipitated in dry Hexane. The salts were filtered off and dried in a vacuum oven at 40°C.

Yields: 90-95%

Nucleophilic substitution reaction. 1g (16 mmol) of PVC, 16 mmol of the thiol compound, 24 mmol of potassium carbonate and 4 mmol tetrabutyl ammonium bromide (TBAB) were dissolved in 100ml of the respective solvent and allowed to react at temperature and reaction time indicated in table 1. (In the cases of modification with thiolates, no potassium carbonate was used). The reaction mixture was then precipitated in cold methanol, purified with THF-methanol as solvent-precipitated system and dried at 50°C for two days.

Results and discussion

Substitution of chlorine atoms in the PVC chains requires strongly nucleophilic agents. The basicity of this compounds, however, should be low to evoid undesired dehydro chlorination. In order to find the conditions which favor substitution of the chlorines by the thiol group to a maximum extent and suppress at the same time substitution by the second functionality (where this is possible) the parameters like solvent, temperature, reaction time, base and thiol type (aliphatic or aromatic) were varied. The experimental conditions used in the modification reaction are listed in table1.

The obtained polymers were isolated, dried and analyzed by means of H-NMR and IR in order to calculate conversions and evaluate compound selectivity and extent of side reactions.

From the results which are summarized in table 2 some general conclusions can be drawn. It can be seen that the best results concerning purity and degree of substitution of the polymers are obtained with aromatic thiols. NMR-spectra of PVC modified with aliphatic thiols always show a considerable amount of olefinic double bonds due to HCl elimination. Consequently these products are colored.

Attempts to introduce a carboxy group into the PVC chain failed. Obviously, its nucleophilic reactivity is comparable to that of the thiol because only crosslinked products were obtained. Hydroxy groups, however, do not react under the given conditions as nucleophiles. In the case of reactions **12** and **13**, where 2-mercapto benzylalcohol and 4-mercapto benzylalcohols are used as modification agents the free hydroxygroups in the polymer can be detected by H-NMR,as it is shown in a recent paper (7). In reaction **5** the corresponding proton signal is covered by other signals but can be detected by IR.

Nitro groups at the aromatic system (**10,11**) of the thiol compounds reduce notably the electron density and with this the nucleophilicity of the sulfur. Comparably low conversions are the consequence.

Table 1: Reaction conditions for the substitution reaction with PVC

Thiol compound	No	Solvent	Base	Temp	time
R_1-CH_2-SH	**3a**	C.H.	K_2CO_3	60°	24h
R_1-CH_2-SH	**3b**	DMSO	K_2CO_3	45°	24h
R_2-CH_2-SH	**4a**	C.H.	K_2CO_3	60°	24h
R_2-CH_2-SH	**4b**	DMSO	K_2CO_3	45°	24h
R_3-CH_2-SH	**5a**	C.H.	K_2CO_3	60°	18h
R_3-CH_2-SH	**5b**	DMSO	K_2CO_3	45°	1h
R_4-CH_2-SH	**6a**	C.H.	K_2CO_3	60°	12h
R_4-CH_2-SNa	**6b**	C.H.	-	60°	2min
R_5-SH	**7a**	C.H.	K_2CO_3	60°	24h
R_5-SH	**7b**	DMSO	K_2CO_3	45°	12h
R_6-SH	**8a**	C.H.	K_2CO_3	60°	48h
R_6-SH	**8b**	DMSO	K_2CO_3	60°	48h
R_6-SNa	**8c**	C.H.	-	60°	24h
R_7-SH	**9a**	C.H.	K_2CO_3	60°	48h
R_7-SNa	**9b**	C.H.	-	60°	48h
R_7-SNa	**9c**	DMSO	-	20°	48h
R_8-SH	**10a**	C.H.	K_2CO_3	60°	48h
R_8-SH	**10b**	C.H.	-	60°	48h
R_9-SH	**11a**	C.H.	K_2CO_3	60°	48h
R_9-SH	**11b**	DMSO	K_2CO_3	45°	24h
R_9-SNa	**11c**	C.H.	-	60°	48h
R_{10}-SH	**12**	C.H.	K_2CO_3	60°	24h
R_{11}-SH	**13**	C.H.	K_2CO_3	60°	48h

R_1	R_2	R_3	R_4
-COONa	-CH_2-COOH	-CH_2 - OH	-CH_2 - O -

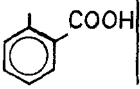
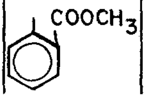
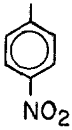
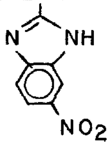
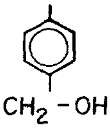
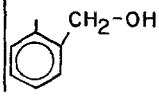
R_5	R_6	R_7	R_8	R_9	R_{10}	R_{11}
						

Table 2: Results of the substitution reaction with PVC

No	color	conversion	observation
3a **3b**	orange orange	not determined	crosslinked crosslinked
4a **4b**	orange orange	not determined	crosslinked crosslinked
5a **5b**	orange orange	18% 25%	considerable elimination considerable elimination
6a **6b**	dark yellow black	11% -	considerable elimination degradation
7a **7b**	yellow orange	not determined	crosslinked crosslinked
8a **8b** **8c**	white yellow white	23% 27% 35%	no side reaction little elimination no side reaction
9a **9b** **9c**	white white white	18% 55% 20%	no side reaction no side reaction no side reaction
10a **10b**	yellow yellow	3% 25%	no side reaction no side reaction
11a **11b** **11c**	white yellow yellow	0% 4% 8%	no reaction at all little elimination little elimination
12	white	55%	no side reaction
13	white	11%	no side reaction

Conclusions

In the present work it was shown that different functional groups can be introduced into PVC chains by chemical modification with bifunctional thiol compounds. Best results are obtained using para-substituted aromatic agents which lead to chlorine substitution degrees of up to 50%. Side reactions are not observed.

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