

CARBONATE CATALYZED NUCLEOPHILIC SUBSTITUTION OF POLY(VINYL CHLORIDE)

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Abstract

Poly(vinyl chloride) was modified by the nucleophilic substitution with iminodiacetic acid dimethylester and n-decathiol. The reaction took place in dimethylformamide and cyclohexanone with K_2CO_3 as a catalyst. Under the conditions used, the direct substitution with iminodiacetic acid was not successful; however, the acid might be accessible by the hydrolysis of the ester. The modification changed properties of the original polymer. It is expected that the iminodiacetic acid modified PVC can be used as a cationic ion exchanger. n-Decathiol modified PVC might have the properties of flexible PVC.

Keywords: Iminodiacetic acid; Iminodiacetic acid dimethylester; n-decathiol; PVC modification

1. Introduction

Modification of waste poly(vinyl chloride) (PVC) is one possibility for the utilization of waste plastics. Nucleophilic substitution is applicable to rigid and flexible PVC, as well [1, 2]. Various groups can be introduced into the polymer. Especially amines and thiols have proven to be appropriate nucleophiles. The substitution of chlorine by isothiocyanate resulted in an antibacterial active material [3]. In this work it was tried to introduce another two groups, iminodiacetic acid and n-decathiol, into the polymer matrix (Fig. 1).

Iminodiacetic acid is well known as a chelater. It might be possible to convert used PVC into a polymer with cationic ion exchange properties, if iminodiacetic acid is introduced.

The introduction of long-chain aliphatic thioether groups into the polymer matrix would weaken the interaction between polymer chains. Therefore, it can act as a plasticizer for a new kind of flexible PVC without the risk of releasing monomeric plasticizer molecules.

2. Materials and Methods

Plain PVC powder was used in order to avoid effects from foreign materials. K_2CO_3 was also provided from Wako Chemicals. Solvents, iminodiacetic acid, and n-decathiol were delivered from Kanto Chemicals. Iminodiacetic acid dimethylester was prepared by the esterification of iminodiacetic acid with methanol. The sodium salt of iminodiacetic acid dimethylester was obtained by the reaction of sodium hydride with the dimethylester. Water was removed from all the chemicals used in order to avoid the introduction of hydroxyl-groups into the modified PVC.

The modification of PVC was carried out in a three neck flask at 100 °C in dimethyl formamide and cyclohexanone, respectively. 1.0 g of PVC was dissolved in 50 ml solvent and 16 mmol of nucleophile and 1.11 g of K_2CO_3 was added as a catalyst. After a reaction time of 4 h, the product was precipitated by the addition of a methanol/water mixture, filtrated, and dried.

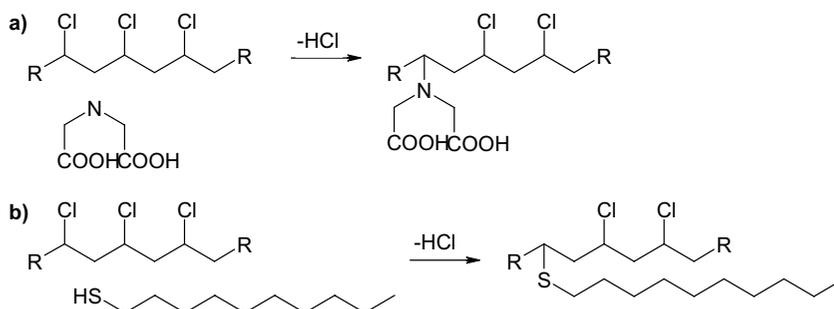


Fig. 1. Nucleophilic substitution of PVC with a) iminodiacetic acid and b) n-decathiol.

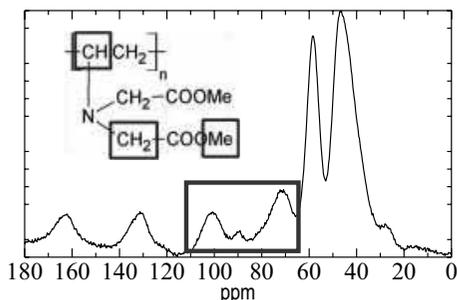


Fig. 2. ¹³C-NMR of iminodiacetic acid dimethylester modified PVC

Substitution and elimination yield were calculated from ¹H-NMR data.

3. Results and Discussion

The nucleophile substitution of PVC with iminodiacetic acid, iminodiacetic acid dimethylester, and the iminodiacetic acid dimethylester sodium salt was carried out in dimethyl formamide. ¹³C-NMR (Fig. 2) showed the successful introduction of the dimethylester in the polymer, while the acid did not show any reactivity (Table 1), probably due to the reduced nucleophilicity by the mesomeric effect of two neighboring acetyl-groups. The effect of sodium salt was weaker as that of the K₂CO₃ catalyzed reaction. The elimination of about 10% of the chlorine during the reaction with iminodiacetic acid was probably the result of the addition of K₂CO₃ as a catalyst and not caused by the nucleophile.

n-Decathioether groups were successfully introduced into the PVC polymer using cyclohexanone as a solvent. From the ¹H-NMR (Fig. 3), it can be seen that about 2.5% of the chlorine was substituted by n-decathiol (Table 1). Another 9% of the chlorine was eliminated. Since no change in the color was observed, it can be assumed that the length of cumulated double bonds was limited.

The introduction of n-decathioether groups had a noticeable effect on some properties of the material.

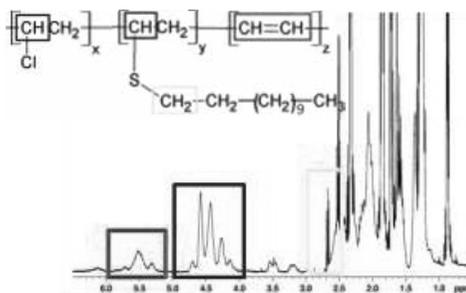


Fig. 3. ¹H-NMR of n-decathiol modified PVC

Compared with the original PVC sample, the solubility of the modified PVC was significantly improved in some solvents such as chloroform.

4. Conclusions

The modification of PVC with iminodiacetic acid dimethylester and n-decathiol results in a polymer with different properties compared with the original polymer. Even if iminodiacetic acid cannot be introduced directly, the acid modified polymer is accessible by the hydrolysis of the ester, in order to make use of its capacity as a chelating agent.

The modification of PVC with n-decathiol caused also changes in the properties of the original material.

References

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Table 1. Substitution and elimination yield of various nucleophiles.

Nucleophile	Substitution [%]	Elimination [%]	Solvent
Iminodiacetic acid	-	10	Dimethyl formamide
Iminodiacetic acid methyl ester	3.6	29	Dimethyl formamide
Iminodiacetic acid dimethyl ester sodium salt	2.8	36	Dimethyl formamide
n-Decathiol	2.5	8.8	Cyclohexanone