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# MODIFICATION OF PVC WITH LONG ALKYL CHAINS BY NUCLEOPHILIC SUBSTITUTION

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## Abstract

We investigated modifying poly(vinyl chloride) (PVC) by with long alkyl chains by nucleophilic substitution with layered double hydroxides(LDH) as basic catalysts. The degrees of substitution and elimination were analyzed by  $^1\text{H-NMR}$ . PVC reacted not only with thiols and alcohols, but also with amines and carboxylic acids. Derivatives of thioglycolic acid reacted with PVC in a high degree of substitution. In cyclohexanone, reactivity was very low, but substitution selectivity was extremely high. On the other hand, in *N,N*-dimethylacetamide (DMAc), reactivity was higher than cyclohexanone but elimination reaction also occurred. Thermal stabilities of the modified PVC were analyzed by TG/DTA. LDH intercalated with various anions ( $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ) was used, and the LDH intercalated carbonate displayed the highest reactivity. LDH made by various hydroxides was used, and while Mg-Al and Li-Al LDH worked as catalysts, the reaction was not observed with Cu-Al or Zn-Al LDH.

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**Keywords:** Poly(vinyl chloride), Nucleophilic substitution, Layered double hydroxides

## 1. Introduction

Poly(vinyl chloride) (PVC) is a plastic that has many exceptional properties like thermal resistance, durability and workability. Therefore, it is used for pipes, cables, medical use bags, etc. Some waste PVC is recycled, but seriously degraded PVC and composite materials are landfilled because recycling is difficult. To promote resources recycling, a new way of recycling is necessary. One option is upgrade recycling. It is a way of recycling that consists in dechlorinating PVC and introducing other functional groups by substitution reaction [1]. We achieved addition of antibacterial properties to PVC by nucleophilic substitution in an earlier paper [2]. New functions added to PVC differ depending on the nucleophile. If nucleophiles with long alkyl chains are added, an increase of plasticity is expected. In this reaction, a base is needed to cause substitution. However, not only substitution but also elimination occurs by the base. To restrain elimination, we used layered double hydroxides (LDH) as basic catalysts. LDH consists of positively charged brucite-like layers  $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}$  alternating with disordered, negatively charged interlayers  $[\text{A}_{x/n} \cdot n\text{H}_2\text{O}]^{x-}$ . Since the basic anion is trapped within the interlayers, PVC polymer can not be in contact with the anion. In this study, we investigated modifying PVC with long alkyl chains by nucleophilic substitution with LDH as basic catalysts from a standpoint of upgrade recycling.

## 2. Materials and Methods

### 2.1. Materials

Plain PVC powder was used in order to avoid effects from foreign materials. Solvent and nucleophile were also

provided from Kanto Chemicals. LDH was prepared by coprecipitation method.

### 2.2. Methods

PVC (0.5 g, 8 mmol) and nucleophile were dissolved in 50 ml of solvent. LDH was added and the reaction started under  $\text{N}_2$  atmosphere at 80 °C. After reaction, LDH was removed by filtration. The mixture was precipitated in methanol or hexane. The modified polymer was purified using THF/hexane as a solvent-precipitant system. The modified PVC was analyzed by  $^1\text{H-NMR}$ , FT-IR, and TG/DTA. The LDH was analyzed by XRD.

## 3. Results and Discussion

### 3.1. The effect of the nucleophiles

The degree of substitution and elimination of PVC modified with various nucleophiles are summarized in Table 1. Without LDH, the reaction was not observed. This result indicates that LDH acts as a catalyst in this reaction. In cyclohexanone reactivity was very low, but substitution selectivity was extremely high. On the other hand, in *N,N*-dimethylacetamide (DMAc), reactivity was higher than in cyclohexanone but elimination reaction also occurred. No effects from the chain length of the alkyl thiols were observed. In the case of using derivatives of thioglycolic acid, the degree of substitution improved. The reason for that is that the carbonyl group in the beta-position withdrew electrons and stabilized the thiolate anion. PVC reacted not only with thiols and alcohols, but also with amines and carboxylic acids.

Table 1. The degree of substitution and elimination of PVC modified with various nucleophiles.

Nucleophile	Solvent	LDH	Substitution (%)	Elimination (%)
1-Dodecanethiol	Cyclohexanone	○	1.6	n.d.
		×	n.d.	n.d.
	DMAc	○	6.6	4.2
		×	n.d.	n.d.
1-Octanethiol	Cyclohexanone	○	1.6	n.d.
	DMAc	○	5.0	6.5
1-Hexadecanethiol	Cyclohexanone	○	2.1	n.d.
	DMAc	○	3.0	7.1
Isooctyl thioglycolate	Cyclohexanone	○	2.3	n.d.
	DMAc	○	17.8	3.9
Stearyl thioglycolate	DMAc	○	12.8	4.4
1-Dodecanol	DMAc	○	2.0	n.d.
Dodecylamine	DMAc	○	5.8	6.8
Tridecanoic acid	DMAc	○	2.4	7.1

### 3.2. Analysis of the pyrolysis substituted PVC

In Fig. 1, the TGA/DTA of pure PVC and PVC modified with various nucleophiles are compared. The pyrolysis behavior of the substituted PVC with 1-dodecanethiol and isooctyl thioglycolate was almost the same as for pure PVC. However the temperature of the start of dechlorination ( $T_{D-onset}$ ) fell as substitution and elimination reactions were promoted. Cl<sup>-</sup> groups decreased by substitution and elimination during the PVC modification, causing a lower degradation temperature. In the case of PVC substituted with 1-dodecylamine, dechlorination temperature decreased greatly. It is assumed that the elimination of the amino group took place first, and then the eliminated amine attacked PVC. As a result, dechlorination reaction was promoted.

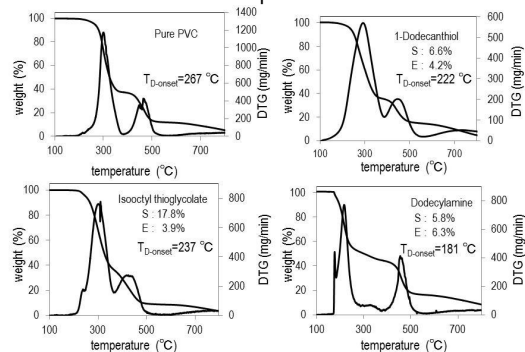


Fig.1 TG/DTA of modified PVC.  
(S: substitution, E: elimination)

### 3.3. The effect of the anions intercalated in LDH

The degree of substitution and elimination of PVC reacted with LDH intercalated various anions are summarized in Table 2.

Table 2. The degree of substitution and elimination of PVC reacted with LDH intercalated various anions.

(Solvent: DMAc, Nucleophile: 1-Dodecanthiol)

LDH type	Substitution(%)	Elimination(%)
LDH- CO <sub>3</sub>	6.6	4.2
LDH- OH	4.0	4.5
LDH- NO <sub>3</sub>	n.d.	n.d.

The LDH intercalated with carbonate showed the highest reactivity. Therefore, it was observed that intercalated anions played an important role in the reactivity.

### 3.4. The effect of the hydroxides in LDH

The degree of substitution and elimination of PVC reacted with LDH made by various hydroxides are summarized in Table 3. Mg-Al and Li-Mg LDH worked as catalysts, but the reaction was not observed with Cu-Al or Zn-Al LDH. It depended on the solubility product ( $K_{sp}$ ) of carbonate. The small solubility product ( $K_{sp}$ ) of carbonate indicates that bonding strength between metal ion and carbonate is strong and therefore, the reactivity of carbonate is small.

Table 3. The degree of substitution and elimination of PVC reacted with LDH made by various hydroxides.  
(Solvent: DMAc, Nucleophile: 1-Dodecanthiol)

LDH type	Substitution(%)	Elimination(%)
Mg-Al	6.6	4.2
Li-Al	14.2	8.9
Cu-Al	n.d.	n.d.
Zn-Al	n.d.	n.d.

## 4. Conclusions

PVC modified with nucleophiles with long alkyl chains was obtained by nucleophilic substitution. In the case of using derivatives of thioglycolic acid, the degree of substitution improved. Additionally, the modification of PVC caused a lower degradation temperature. Lastly, it was observed that the intercalated anions and hydroxides played an important role in the reactivity.

## References

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