

어택틱 폴리프로필렌의 화학적 개질—어택틱 폴리프로필렌의 포스포닐화

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Chemical Modification of Atactic Polypropylene —Phosphonylation of Atactic Polypropylene

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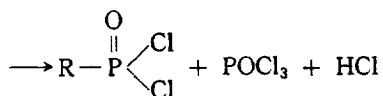
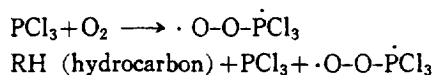
요약 : 어택틱 폴리프로필렌을 삼염화인과 산소와 반응시켜 포스포산 혹은 포스포산에스테르 치환기를 갖는 중합체를 합성하였다. 인의 함량이 8% 이상 되도록 반응시킬 수 있었으며 포스포산에스테르기를 갖고 있는 중합체는 어택틱 폴리프로필렌보다 클로로포름이나 테트라히드로퓨란과 같은 유기용매에 대하여 좋은 용해도를 보여주었다. 포스포닐화반응에서 치환도가 클수록, 다시 말하면 반응시간이 길수록, 또 어택틱 폴리프로필렌의 농도가 짙을수록 불용성 부분의 양이 증가함을 관찰하였다.

Abstract: Atactic polypropylene could be chemically modified to contain phosphonic acid or phosphonic ester pendant groups by phosphonylation using phosphorus trichloride and oxygen. More than 8% of phosphorus could be incorporated into the polymer. Polymers containing phosphonic ester group showed better solubility in polar organic solvents such as chloroform and tetrahydrofuran. The amount of insoluble portion increased with reaction time or degree of phosphonylation and with the concentration of atactic polypropylene.

INTRODUCTION

The method of oxidative chlorophosphonylation of hydrocarbons using phosphorus trichloride

and oxygen has been applied to various polymeric systems in order to incorporate phosphonic acid and their derivatives as pendant groups¹⁻⁶. Soborovskii et al.⁷ proposed a free radical mechanism for such reaction:



The initial product, phosphonyl dichloride, can be readily converted subsequently either to acid by hydrolysis or to esters or amides by esterification or amidation. Isbell and Wadsworth⁸ performed a detailed study on the effect of various factors on this reaction. Schroeder and Sopchak³ studied the phosphonylation of polyethylene grease by applying the same method and could introduce 7-16% of phosphorus into the polymer. Recently Weiss et al.⁵ examined thermal and mechanical properties of polyethylene modified by the inclusion of phosphonic ester pendant groups.

The purpose of the present work is to study the phosphonylation of atactic polypropylene using phosphorus trichloride and oxygen and the results are reported in this paper.

EXPERIMENTAL

1. Materials

Atactic polypropylene of average molecular weight of about 2000 was obtained from Korea Petrochemical Ind. Co. & Ltd. and used as received for the present work. When the sample was subjected continuous Soxhlet extraction with benzene for 24 hrs., 2.9wt. % of insoluble residue was left in the thimble. Other chemicals employed in this study were of reagent grade and used without further purification.

2. Phosphonylation Procedure

Atactic polypropylene (10.0g) and various amounts of phosphorus trichloride (Table I) were placed in a three-necked round-bottom flask equipped with a gas inlet tube, dry-ice/ethanol

reflux condenser, and a thermometer. After the mixture was purged with dry nitrogen, oxygen was allowed to bubble through the homogeneous reaction mixture with a flow rate of 110cc/min. The gases were dried by passing through concentrated sulfuric acid and calcium chloride calcide tube.

The reaction mixture was continuously stirred during the reaction. When oxygen was allowed to bubble through, temperature of the mixture slowly rose to about 55°C. We have, however, maintained the reaction temperature at 58°C throughout the reaction. Reaction mixtures were initially heated to 58°C in a water bath and then oxygen was allowed to bubble through.

3. Separation of Polymers with Phosphonic Acid and Phosphonic Ester Pendant Groups.

At the end of each reaction the volume of reaction mixture was reduced to one-half of its original volume by distilling off phosphorus trichloride and phosphorus oxychloride at 80°C under a reduced pressure (12mmHg).

Then the mixture was slowly poured into either excess amount of cracked ice or a dry and chilled alcohol containing enough quantity (ca. 30% by volume) of pyridine. The whole mixture was allowed to stand for 24 hours at room temperature.

The precipitated polymers were collected by filtration and thoroughly washed with distilled water or alcohol used for esterification followed by ethanol. The washed polymers were dried at 40°C under a reduced pressure (10mmHg).

4. Determination of Phosphorus Content

Contents of phosphorus in the polymers were determined colorimetrically following the well-known procedure.⁹ Polymers (10-20mg) were decomposed in a hot concentrated sulfuric and nitric acid mixture. The clear solution was then

Table I. Phosphonylation of Atactic Polypropylene*¹

Exp. No.	Reaction Time (hrs.)	Phosphorus Content (wt. %)	Degree of Substitution* ²	Insoluble Portion (wt. %)
1	3	2.8	73.4	3.7
2	5	4.3	45.8	3.9
3	7	8.3	21.0	4.1
4	9	8.5	20.0	5.2

*¹ Phosphonylation was conducted at the reactant ratio of 20 : 1 (w/w) of phosphorus trichloride and atactic polypropylene. All the data are for phosphonic acid group containing polymers.

*² Average number of carbon atoms per phosphonic acid functional group.

Table II. Effect of Reactant Ratio in Phosphonylation*¹

Exp. No.	Reactant Ratio (w/w)	Phosphorus Content (w. %)* ²	Degree of substitution* ³	Insoluble Portion (wt. %)
1	20 : 1	8.3(8.1)	21.0	4.1
2	10 : 1	6.6(5.7)	27.8	9.7
3	20 : 3	5.4(4.3)	35.3	14.5

*¹ All the data are for phosphonic acid group containing polymers. Phosphonylation was conducted for 7 hrs. Reactant ratio=wt. of phosphorus trichloride/wt. of atactic polypropylene

*² Values in parentheses are for insoluble portions.

*³ Same as in Table I

treated with sodium sulfite. Color of the solution was developed using ammonium molybdate-hydrazine solution. A calibration curve was constructed using triammonium phosphate as a standard. Blank test was run for each analysis.

RESULTS AND DISCUSSION

1. Phosphonylation Reaction

When the reactant ratio of 20 : 1 (w/w) of phosphorus trichloride and atactic polypropylene was employed for phosphonylation and the resulting product was hydrolyzed to acid form, the degree of phosphonylation increased with reaction time (Table I). The reaction, however, slowed down after 7 hrs. of reaction. The average degree of substitution at this point was one phosphonic acid group per 21 carbon atoms, i. e., 7 propylene units.

Table I also shows the fact that the amount

of benzene insoluble portion, determined by Soxhlet extraction for 24 hrs., increased with reaction time as well as with the degree of substitution. The insoluble portion seemed to be of crosslinked structure and did not fuse on heating.

Variations in reactant ratio resulted in changes not only in degree of substitution but also in the amount of insoluble gels (Table II). The higher was the concentration of atactic polypropylene, the lower the degree of phosphonylation, which must be due to a simple concentration effect. Higher concentration of atactic polypropylene also gave rise to larger amount of the insoluble, although the degree of substitution was lower. This phenomenon seems to occur due to higher chance for interchain free radical coupling reactions. Free radical nature of this type reactions was earlier demonstrated by many workers^{7,8}. Table II also shows that the degree

Table III. Phosphorus Contents of Atactic Polypropylene Containing Phosphonic Ester Pendant Groups

Exp. No.	Ester Derivatives	Phosphorus Content (wt. %)	
		Found	Calculated
1	acid	8.3	—
2	ethyl ester	7.5	7.6
3	butyl ester	6.4	6.7
4	cyclohexyl ester	5.8	6.1
5	phenyl ester	6.1	6.2
6	benzyl ester	5.9	6.0
7	isooctyl ester	5.1	5.2

Table IV. Solubility of Modified Polymers*

Solvent	THF	Chloroform	Benzene	Ethyl Chloride	Dioxane	Diethyl Ether	Acetone
Polymers							
original polymer	×	×	○	×	×	△	×
acid form	△	△	△	×	×	×	×
ethyl ester	○	△	△	△	×	×	×
butyl ester	○	○	△	△	△	×	×
cyclohexyl ester	○	○	△	△	△	×	×
phenyl ester	△	○	△	×	×	×	×
benzyl ester	△	○	△	△	×	×	×
isooctyl ester	○	△	△	×	×	×	×

*○; soluble, △; partially soluble or swollen, ×; insoluble

of phosphonylation was lower in the insoluble portions compared with the soluble portions.

Alcohols employed for esterifications were ethyl, n-butyl, cyclohexyl, benzyl, and isooctyl alcohols and phenol.

2. IR Absorption Characteristics of Atactic Polypropylene with Phosphonic Acid Pendant Groups

IR spectrum of atactic polypropylene containing phosphonic acid pendant groups showed characteristic absorptions for P-O-H at 2820 and 2320 cm^{-1} , for P-O-H/P=O combination at 1610-1675 cm^{-1} , and for P=O at 1145 cm^{-1} , which are in close accord with those assigned by Weiss et al. for methylphosphonic acid^{5,8,10,11}. Atactic polypropylene has primary as well as

secondary and tertiary hydrogens which can be substituted by phosphonyl groups. The extent of substitution at each position, however, could not be quantitatively determined, tertiary carbon atoms would be preferred substitution though ituting positions.

3. Atactic Polypropylene with Phosphonic Ester Pendant Groups

Chlorophosonylated atactic polypropylene sample, a part of which was directly hydrolyzed to acid form (Exp. No. 3 in Table I and Exp. No. 1 in Table II), was converted to various esters and the results are summarized in Table III. The calculated phosphorus contents were estimated from that of acid form based on the assumption that all the phosphonyl groups

have been converted to ester groups. These values, as one can see from Table III, are in good agreement with experimental values.

The IR spectra of ester containing polymers showed characteristic strong absorptions for P-O-C functionality at around 1045cm^{-1} and for P=O at 1250cm^{-1} . Absorptions characteristic for P-O-H functional groups were not observed.

Esterified polymers exhibited improved solubility in relatively polar solvents such as chloroform and tetrahydrofuran than atactic polypropylene and phosphonic acid form did (Table IV).

CONCLUSION

Atactic polypropylene could be phosphonylated using phosphorus trichloride and oxygen to various degrees of substitution. The polymers which were modified to have phosphonic ester groups showed better solubility in polar solvents than atactic polypropylene itself and polymers having free phosphonic acid pendant groups. Utilization of these modified polymers flame retardant or polymeric plasticizer applications can be envisaged.

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