

본질적 난연 및 내열성 해테로환식 폴리머의 특성에 관한 연구

A Study on the Characterization of Intrinsic Flame Retardant and Heat Resistant Sulfur-Bridged Heterocyclic Polymers

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ABSTRACT

The intrinsic flame retardant and heat resistant polymers such as PQXS[poly(quinoxaline)sulfide], PIQS[poly(isoquinoline)sulfide] and PQS[poly(quinoline)sulfide] were synthesized from 2, 3-dichloroquinoxaline, 1, 3-dichloroisoquinoline and 4, 7-dichloroquinoline. They were characterized by FT-IR, UV/Vis spectroscopy, DTA and elemental analysis. The melting point above 350°C of the polymers show higher than that of the heat resistant PPS polymer(mp. 295°C). In the LOI test, the polymers exhibit an intrinsically high flame retardant property having the LOI values in the range of 41~42. The vertical burning test for the polymers also show an UL 94 V-0 performance.

국 문 요 약

본질적인 난연 및 내열성의 PQXS, PIQS, PQS 3종류의 폴리머를 2,3-dichloroquinoxaline, 1, 3-dichloroisoquinoline, 4,7-dichloroquinoline을 각각 출발 물질로 하여 합성하였다. 이들을 FT-IR, UV/Vis 분광분석, DTA, 원소분석 등에 따라 특성분석을 행하였다. 이들 폴리머소재는 내열 및 난연특성 시험에서 녹는점 기준 350°C 이상의 높은 내열성과 LOI값 기준으로 41~42의 높은 수치의 난연특성을 나타내었으며 또한 수직연소시험에서 UL 94 V-0 등급의 높은 난연특성을 나타내었다.

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1. INTRODUCTION

We encounter many kinds of engineering plastics in our life. The engineering plastics can displace the metals in industries due to their good mechanical properties and the ease of processability. However, the use of engineering plastics is limited because they can evolve toxic gases and cause damages to the equipments of industries during combustion. Many researchers have studied the development of the heat-resistant engineering plastics and explored the possibilities to retard the flammability of polymers which includes a range of plastics¹⁻³⁾ with specific groups such as sulfur, phosphorus and halogen.

All of the polymers decompose thermally before ignition in the combustion process. The decomposition of polymers depend on their thermal stability. The thermal stability is one of the important factors to evaluate the flame retardant property of the polymer.

The burning of the polymer proceeds in several stages^{4,5)}: heating of the polymer, decomposition, ignition, combustion, and fire propagation.

In the first stage, the solid polymer is heated by flame. The heated polymer, as a thermoplastic, softens or melts and then begin to flow. The subsequent stages are affected by the melting temperature of the polymer in the combustion process. Consequently, gaseous or condensed species are generated from the heated polymer.

Volatile gases or chemically degraded polymer fragments are produced during the decomposition of the polymer. Many polymers decompose predominantly into monomers which are usually flammable at sufficiently high temperatures.

In order the ignition to occur, the temperature of the polymer increases and the flammable gases formed reach an appropriate ratio with respect to the oxygen of the atmosphere. The burning depends on the transfer of sufficient heat from the flame to the polymer to maintain a supply of flammable gaseous decomposition products and a

supply of oxygen from the surrounding atmosphere sufficient to support combustion. In the combustion stage, the energy relationships of the molecules correlate with the characteristics of the polymer. Cohesive energy, hydrogen bonding, heat of combustion and dissociation energy are the most important energy factors. In the fire propagation stage, if the net heat of combustion is sufficient to bring the adjacent mass to the combustion stage, the fire propagation can proceed. Especially for polymeric materials, fire endurance, heat contribution, smoke production and fire gases are also important parameters.

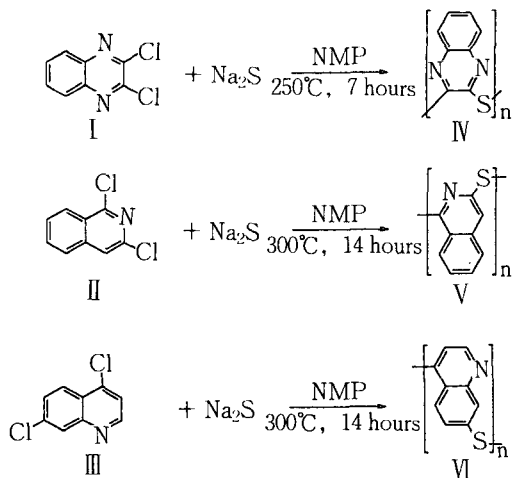
In order to improve the thermal stability of polymers, the methods of halogenation or blend with halogenated materials was adopted. Although the improved plastics are better flame retardant than the crude ones, they can evolve toxic smoke or gases during the combustion process. It has been reported that halogen containing gases or smoke is the most corrosive among the evolved gas or smoke in the burn⁶⁾.

In this work, some new polymers which exhibit thermal stability without halogenation or blend of halogenated materials, i.e. polymers with inherent flame retardant, were synthesized and characterized. The structures of the new polymers are based on the structure of poly(phenylene sulfide) (PPS) as engineering plastics. PPS has a good thermal stability. PPS consists of alternatively sulfur atom and benzene in the polymer unit. In recent years, the use of PPS has increased in the industries due to its good thermal, mechanical properties and self-extinguishing properties, such as UL 94 V-0 rating by Underwriter's Laboratory (UL). PPS compounds can be applied to the injection molding and coating on the metal substrates^{2,7-9)}.

2. EXPERIMENTAL

2,3-Dichloroquinoxaline I, 1,3-dichloroisoquinoline II and 4,7-dichloroquinoline III were used

as starting materials, Na_2S used was anhydrous, and N-methyl-2-pyrrolidone (NMP) was used as solvent. All the starting materials were purified by recrystallization from methanol before use. NMP was dried by removing water in a column packed with glass helices. The synthetic method reported in a U.S. Patent¹⁰⁾ was modified with respect to reaction time, reaction temperature and amount of reactants. The starting materials and anhydrous Na_2S were mixed with NMP in a steel reactor (ROTH model I : Germany). The mixture was heated with stirring. When 2,3-dichloroquinoxaline was used as the starting material, the reaction temperature was 250°C and the reaction time was 7 hours. In the cases of 1,3-dichloroisoquinoline and 4,7-dichloroquinoline, they were 300°C and 14 hours, respectively. This reaction proceed by polycondensation mechanism¹¹⁾. The synthetic schemes are as follows :



Synthetic scheme

The obtained product was washed several times with deionized water to remove NaCl as byproduct and with CH_3OH . In order to remove the oligomers, the product was extracted with acetone in a Soxhlet extractor until the extract was colorless. Consequently, poly(quinoxaline sulfide) [PQXS] IV, poly(isoquinoline sulfide) [PIQS] V and poly(quinoline sulfide) [PQS] VI were obtained.

The polymers were characterized by FT-IR spectra, UV/Vis spectra, and elemental analyses. The thermal stability of the polymers was measured by TG/DTA. FT-IR spectra were recorded on a Bruker (Germany) IFS 48 spectrometer by KBr-pellet technique and a Shimadzu (Japan) UV-2102 PC UV/Vis spectrophotometer was employed for solid state spectroscopic measurements. The elemental analyses of polymers were measured by Carlo Erba Elementaranalyser 1104, 1106 (Germany) and Netzsch Simultan-Thermoanalysegerät STA 409 (Germany) was employed for TG/DTA. The method of LOI (limiting oxygen index) measurement for the polymers was followed ASTM D 2863.

3. RESULTS AND DISCUSSION

The obtained polymers in this work are brownish black powders with low yields(5~10%). All FT-IR spectra of the polymers show the broad specific peaks due to accomplished polymerization as shown in Fig. 1. The result of FT-IR spectroscopy for polymers is similar to that of PPS as represented in Table 1. Yamamoto et al.¹³⁾ reported that FT-IR spectrum of PPS shows one absorption at ca. 825cm^{-1} which is attributed to the C-H out-of-plane vibration of 1,4-disubstituted benzenes.

Table 1 FT-IR spectral data for PQXS, PIQS, PQS and PPS

Compound	Wavenumber(cm^{-1})
PPS ¹²⁾	3062(ν C-H), 1560, 1460(ν C=C), 820(δ C-H)
PQXS	3058(ν C-H), 1579, 1452(ν C=C), 850(δ C-H)
PIQS	3057(ν C-H), 1596, 1436(ν C=C), 827(δ C-H)
PQS	3062(ν C-H), 1548, 1431(ν C=C), 858(δ C-H)

In order to confirm the accomplishment of polymerization, the content of Cl for starting materials and polymers was compared. The calculated value for Cl for starting materials are 35.62% I and 35.80% II, III, respectively. The found contents of Cl for polymers are negligible : 0.02% IV, V and 0.04% VI. The presence of trace of Cl

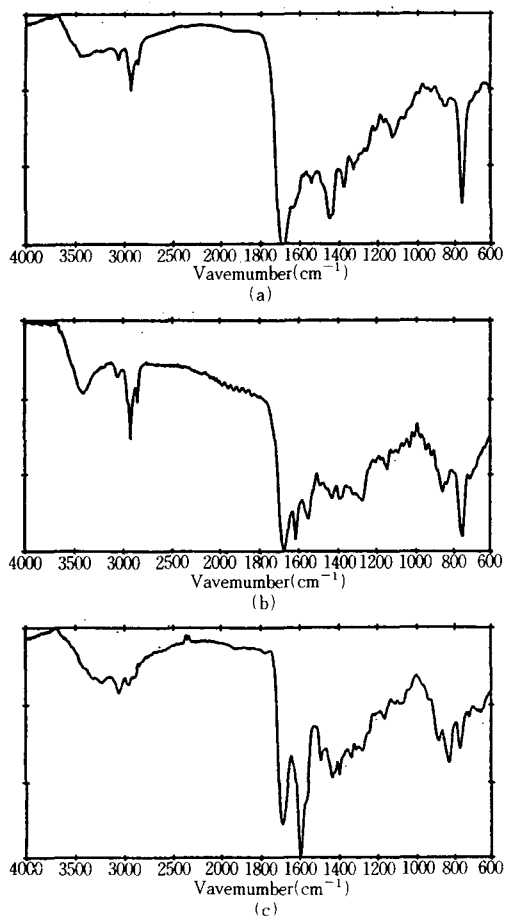


Fig. 1 (a) FT-IR spectrum of PQXS, (b) FT-IR spectrum of PIQS, (c) FT-IR spectrum of PQS

is probably due to the attachment of Cl at the terminal of polymers. Occluded NMP or water present in the polymers can cause some difference between the calculated and experimental values.

The difference of energy absorption between starting materials and polymers can be discovered from the UV/Vis spectra of the products. The starting materials show the following λ_{max} , I : 361, 335, 327, 321 nm, II : 361, 333, 319, 287, 275, 266 nm and III : 322, 309, 275 nm. In the spectra of polymers(IV, V and VI.), the specific peaks of starting materials disappear, and is replaced by broad new peaks at λ_{max} 260~370 nm due to polymerization.

The polymers(IV, V and VI.) do not melt up to 350°C. The melting point of polymers are higher than PPS. Thermal stability which can evaluate the flame retardant and heat resistance of polymers is determined by thermal analysis, e.g. TG/DTA. The scan rate was 30°C/min, and the temperature was increased up to 550°C under nitrogen. The initial decomposition temperature of the polymers were 400~415°C which is lower than PPS but higher than other polymers as represented in Table 2. The residual amount of polymers after TG/DTA measurement were 83.56% IV, 82.76% V and 82.68% VI, respectively.

The LOI of polymers was measured by ASTM D 2863. The LOI of obtained polymers in this work and others polymers also are given in Table 2. The former polymers exhibit an intrinsically high flame-retardant property in the LOI values range of 41~42.

The vertical burning test for the polymers was also carried out by UL 94 V-0. The materials were rated as UL 94 V-0 in section under 1/16 inch.

Table 2 Thermal properties and LOI of various polymers²⁾

Polymer	Melting point (°C)	Initial decomposition temperature (°C)	LOI	Remarks
Polyvinyl chloride	185	200	37~42	ref 2
Polyethylene	130	335	26~27	"
Polypropylene	168	328	25~26	"
PPS	295	494	43~44	"
PQXS	~350	410	41	this work
PIQS	~350	400	42	"
PQS	~350	415	42	"

4. CONCLUSION

The synthesized polymers have the similar unit structure of PPS which have been use widely in industries. The polymers exhibit a good thermal stability as described previously. The enhancement for flame retardant properties and heat resistance of materials was recognized by the introduction of

aromatic groups instead of halogenation or by using blend of halogenated materials which can evolve toxic gases during the combustion process. Consequently, the polymers are inherent flame retardant and are evaluated to generate toxic gas in burn. They also exhibit a more high value for LOI than that of other engineering plastics which is used in industries. The results suggest that the polymers synthesized in this work can find application in the inherent flame retardant plastics in the industries.

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