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論　文　要　旨　(博士)

論文題目	芳香族ポリイミドのシーケンス制御と複合化に関する研究

(要旨　1,200 字程度)

ポリイミド（PI）は、イミド結合を有するポリマーの総称で、高い耐熱性だけでなく、優れた機械強度や電気特性を持っている。その優れた性質から、宇宙航空分野やマイクロエレクトロニクス分野などで使用されている。しかし、使用用途に応じて要求も細分化されており、電子機器の小型化や高性能化、使用される部材の軽量化などから、PI の更なる高性能化が求められている。

本論文では、ポリイミドのシーケンス制御、イミド化温度の低温化およびポリシロキサンとの複合化を行った。

本論文は七章で構成されている。

第一章では、序論として本研究の目的を述べている。

第二章では、従来の可溶性 PI の弱点である耐熱性の低さを克服した新しい可溶性 PI の作製方法を示した。この新規可溶性 PI は、３段階反応で構造を制御したブロック共重合 PI であり、シーケンス制御を行い、アミド交換反応を制御することで耐熱性と可溶性の両立に成功した。新規可溶性 PI が、従来の PI と同等の諸物性を有することを明らかにした。

第三章では、可溶性 PI 特有の問題である塗液の白化について取り上げ、PI の分子構造の制御による方法と添加物を加える方法との２つの手法を用いて、それぞれの解決方法を示した。これらの方法を用いることで、耐白化性を有するだけでなく、高い耐熱性を持つ可溶性 PI が得られることを明らかにした。

第四章では、高温熱処理が必要な PI に可塑剤を用いて、イミド化温度の低温化を試みた。フタル酸エステル、リン酸エステル、ポリエーテル等の可塑剤を用いた。使用した可塑剤の中で、ポリエチレングリコール（PEG）が最も効果的な可塑剤であることを明らかにした。また、PEG を加えたフィルムと無添加フィルムの諸物性を比較した。PEG を加え、低温の熱処理をしたフィルムは、従来の無添加高温熱処理のフィルムと同等の諸物性を有していることを明らかにした。

第五章では、無機高分子のポリジメチルシロキサン（PDMS）を PI 中に分散させるためにゾルーゲル反応を利用し、PI/PDMS ハイブリッドを作製した。ハイブリッドの作製方法およびハイブリッドフィルムの諸物性を示した。その結果、従来の PI に比べ、少量の PDMS とのハイブリッド化することで、フィルムが高性能化していることを明らかにした。

第六章では、ポリシロキサンとして PDMS だけでなく、フェニル基を有するポリメチルフェニルシロキサンおよびポリジフェニルシロキサンを用いた各種 PI/ポリシロキサンハイブリッドを作製し、ハイブリッドフィルムの諸物性を示した。また、ポリシロキサンの構造の違いによ

るハイブリッドフィルムの物性の比較もしている。
　第七章では総括として全体をまとめている。

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Abstract

Title	Study on the sequence control and hybridization of aromatic polyimide

(800 words)

Polyimides (PIs) are important class of aromatic polymers with remarkable heat resistance and superior mechanical, electrical, and durable properties. Because of their excellent properties, PIs have been used in the aerospace, electronics, and various high-tech industries. In the past decade, significant efforts have focused on synthesizing polyimides with further enhanced thermal and mechanical properties. In this study, I prepared aromatic PIs using three methods, sequence control, lowering of the imidization temperature, and hybridization of polysiloxanes.

This paper consists of seven chapters.

In chapter 1, background and aim of this thesis are described.

In chapter 2, soluble PIs which keep high heat resistance were prepared by controlling the molecular structure and sequence. The PI was named 6,6-PI. The meaning of 6,6-PI is the number aromatic rings by using of six first and second steps. The mechanical properties of the 6,6-PI film were as high as those of the existing PI. 6,6-PI also has other advantages as follows. 6,6-PI can be prepared even in the presence of small amount of water, the vanish is stable and preserved at the ambient atmosphere, and films can be processed using the stable imidized form in a short time. Thermal properties were also excellent with high glass transition temperature (T_g), though initial weight loss was slightly larger than existing PI because of the methyl group.

In Chapter 3, the problem of blushing of PI coating fluid typical for soluble PIs was examined. To solve this problem without changing the solvent and without lowering the heat resistance of the soluble PIs, structure control method and additive method were examined. The Solpit-S structure is a typical structure in 6,6-PIs. In the structure control method, hydroxyl groups were found to be effective, and we succeeded in preparing blush resistant 6,6-PIs by introducing Bis(3-amino-4-hydroxyphenyl) Sulfone ($HOSO_2AB$). Blushing time was extended to more than 20 minutes and T_g was higher than 350 °C. In the additive method, DBU type of catalyst (X) was most effective, and the Solpit-S solution containing 10 wt% X showed blushing time more than 30 minutes. The Solpit-S film with 10 wt% X exhibited the same thermal and mechanical properties as the pristine Solpit-S film.

In chapter 4, lowering of the imidization temperature was attempeted by adding various type of plasticizers such as phthalate, phosphate, and polyether. Among them, polyethylene glycol (PEG) was found to be the most effective additive to lower the imidization temperature. Though the imidization of poly(amide acid) (PAA) without plasticizer required high temperature up to 350 °C, in the presence of 5 wt% of PEG, the imidization almost completed at 200 °C. The PEG was removed at around 250 °C, giving pristine PI film. The PI film with 5 wt% PEG, after cured at 250 °C, exhibited the same thermal and mechanical properties as the pristine PI film cured at 350 °C.

In chapter 5, PI / polydimethylsiloxane (PDMS) hybrid was prepared by sol-gel method to disperse PDMS into PI. The method of preparing the PI / PDMS hybrid by combining the in situ sol–gel reaction of precursor PDMS and the thermal imidization of PAA are shown. The obtained hybrid films were transparent when the PDMS content was less than 3 wt%. The hybrid films with up to 3 wt% PDMS showed higher tensile strength and elongation at break than those of pristine PI due to the toughening effect of PDMS. Interestingly, the tensile modulus also increased by the increase of PDMS content up to 3 wt%. The thermal stability of the hybrids also increased with the PDMS content, as evidenced by TGA. In the present chapter, the binary PI / PDMS

with the PDMS content, as evidenced by TGA. In the present chapter, the binary PI / PDMS hybrid containing 3 wt% PDMS showed the best balance of properties including transparency, modulus, toughness, and thermal stability.

In chapter 6, polysiloxanes having phenyl group such as polymethylphenylsiloxane (PMPS) and polydiphenylsiloxane (PDPS) were used to prepare PI / polysiloaxne hybrids. The method of preparing the PI / polysiloxane hybrid and properties of the hybrid film are shown. Tensile strength and thermal stability of PI were increased by the addition of small amount of polysiloxane. The effect of structure of the polysiloxanes on the hybrid films was investigated. The compatibility of hybrids were increased by using PMPS and PDPS than PDMS. In the present chapter, PI / PDPS hybrid showed the highest of properties including transparency and thermal stability.

In chapter 7, summary of this thesis is described.