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Title	α-トルキシル酸誘導体を用いた 官能性バイオベースポリマーの合成
Author(s)	渡辺, 尚登
Citation	
Issue Date	2017-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/14203
Rights	
Description	Supervisor:金子　達雄, マテリアルサイエンス研究科, 修士

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Syntheses of functional bio-based polymers using α-truxillic acid derivatives

Kaneko lab.
1530060
Naoto Watanabe

1. Introduction

Plastics are indispensable to our lives. However, fossil fuel as its raw material is known as the cause of global warming. Using a bio-based raw material will realize a low-carbon society in the future. Generic bio-based polymers such as polylactic acid have low heat resistance because it has Aliphatic backbone. Therefore, I focused on 4-hydroxycinnamic acid (4HCA) as a raw material. It is a rigid structure with photoreactive double bonds and aromatic rings. And it is a metabolic intermediate of lignin biosynthesis and can be artificially synthesized by reacting tyrosine with tyrosine ammonia-lyase (TAL). Our laboratory succeeded in synthesizing highly heat-resistant polyester using 4HCA. The existence of double bond in the polymer induces photodimerization and cis-trans isomerization, and demonstrated the possibility of application to functional materials such as optical and mechanical materials and shape memory materials.

By irradiating 4HCA with ultraviolet light, 4,4'-dihydroxy-α-truxillic acid (4HTA) can be easily synthesized. 4HTA has two hydroxy groups and two carboxy groups, and if one functional group is used for syntheses, the other functional group remains in the side chain. Due to the presence of functional groups in the side chains, solubility of polymers and polymer reactions can be improved, and so 4HTA is very valuable as a bio-based material. In this study, I synthesize two functional bio-based polymers by using 4HTA as a raw material. Furthermore, measurement of various physical properties of the synthesized polymers and polymer reaction give side chain functional group effect.

2. Experimental Section

2-1. Bio-based polycarbonate

Melt polymerization with diphenyl carbonate was adopted as a method for synthesizing polycarbonate. However, since the melting point of 4HTA is higher than the decomposition temperature, melt polymerization can't be carried out. Therefore, a novel functional bio-based polycarbonate **4** was synthesized using 4,4'-dihydroxy-α-truxillic acid methyl ester (4HTA methyl ester) in which 4HTA was methyl esterified.

2-2. Bio-based polyamides

In our laboratory, we synthesized a diamine / dicarboxylic acid compound using 4-aminocinnamic acid (4ACA) as a raw material and bio-based polyamide was synthesized using them as monomers. Novel functional bio-based polyamide **15** using 4,4'-diamino-α-truxillic acid methyl ester (4ATA methyl ester) and 4HTA was synthesized. Syntheses of polyamides **16, 17** using α-truxillic acid (TA) or 3,3'-dihydroxy-α-truxillic acid (3HTA) was also carried out in the same method.

2-3. *O*-Acetylation of 15

O-acetylation of **15** was carried out using acetic anhydride, pyridine and NMP.

2-4. Preparation of carbon fiber reinforced plastics (CFRP)

CFRPs was prepared using **15** and **19** obtained by *O*-acetylation of **15**.

3. Results and Discussion

3-1. Bio-based polycarbonate

Thermal properties

The glass transition temperature was about 30 ℃ lower than conventional polycarbonate. This is thought to be due to a decrease in the intermolecular force because side chains are bulky as compared with side chains of conventional polycarbonate.

Solubility test

Compared to conventional polycarbonate, **4** has high solubility in polar solvents such as ethyl acetate, methanol, dimethyl sulfoxide. In addition, it did not have solubility in nonpolar solvents such as hexane and toluene. From this, it is considered that the polarity of the side chain methyl ester improves the solubility in these polar solvents.

Mechanical properties

4 fiber was prepared by heating to the glass transition temperature. Using this fiber, a tensile test was carried out. Strength, Young's modulus and elongation at break were inferior to conventional polycarbonate. As mentioned above, the side chain functional group is bulky and the intermolecular force is considered to be lower than that of conventional polycarbonate.

3-2. Bio-based polyamides

Thermal properties

15, **16** and **17** showed very high decomposition temperatures. This is considered to be a rigid structure in which aromatic rings, amide bonds, cyclobutane rings are continuous and the stacking of aromatic rings is one factor. In addition, the glass transition point of **15** and **17** exceeded the decomposition temperature. From these results, it is conceivable that the hydroxyl group on the side chains has an effect of reducing the distance between polymer chains by non-covalent bonding, thereby improving intermolecular force and promoting partial physically cross-linking.

Solubility test

15, **16**, **17** were tested for solubility using various organic solvents and concentrated sulfuric acid. Initially, I thought that the polarity of the side chain hydroxyl group would improve the solubility in organic solvents. However, **15**, **17** showed lower solubility in organic solvent than **16**. In addition, the p-hydroxy group showed lower solubility than the m-hydroxy group. As described above, this results is considered to be due to reduction of the distance between polymer chains by side chain hydroxy groups and partial physically cross-linking. Furthermore, these effects were found to be higher for p-hydroxy groups than for m-hydroxy groups.

Mechanical properties

Cast film was cut into rectangular slices and mechanical strength was measured. Comparing **15**, **16** and **17** both strength and Young's modulus increased in the order of **16** < **17** < **15**. As mentioned above, hydroxyl groups bring polymer chains close to each other, improves the intermolecular force, and its effects increases at the p-position.

Optical properties

For measurements of transmittance, cast films prepared by dissolving in DMF was used. All three polymers were highly transparent, equivalent to polycarbonate and Polymethyl methacrylate (PMMA), which are said to be transparent plastics. This transparency is due to the fact that the conjugated system derived from aromatic rings and vinylene structures is interrupted by cyclobutane rings.

3-3. Polyamide 4

NMR spectra

From the NMR spectrum, it was found that **15** was *O*-acetylated. **19** was obtained as a gel-like solid.

Thermal properties

As results of O-acetylation of hydroxy groups, the heat resistance was lowered. It is considered that the side chain became bulky due to the modification of hydroxy groups, and the distance between the polymer chains was opened. Therefore, the intermolecular force decreased.

Solubility test

Solubility tests of **19** in various organic solvents and concentrated sulfuric acid were conducted. It was only slightly soluble in dimethylsulfoxide and concentrated sulfuric acid. Before the modification of hydroxy groups, it showed solubility in the amide type solvent, but after the modification it showed insolubility. This indicates that hydroxy groups have higher affinity with amide type solvents as compared with other solvents.

3-4. CFRP

Mechanical properties

Compared to **15**, CFRP using **15** has greatly improved strength and young's modulus. When CFRP was made with **19** *O*-acetylated with hydroxy groups, both strength and Young’s modulus were lower than CFRP using **15**. It is considered that this is because side chain hydroxy groups interact more strongly with the surface structure of the carbon fibers.

4. Conclusion

Novel functional bio-based polycarbonate **4** was synthesized using 4HTA methyl ester. Due to the bulkiness of side chain methyl esters, heat resistance and mechanical strength were inferior to conventional polycarbonate. However, due to the polarity of the methyl ester, the solubility in the polar solvent was increased as compared with the conventional polycarbonate. Three new functional bio-based polyamides **15**, **16**, **17** were synthesized using 4HTA and 3HTA, TA and 4ATA methyl ester. By heat resistance measurement, it was found that side chain hydroxyl groups reduce the distance between polymer chains, giving intermolecular force improvement and partial physical crosslinking. Also, by the solubility test, it was found that p-hydroxy groups had this effect higher than m-hydroxy groups. As a result of NMR measurement, it was found that *O*-acetylation of **15** was successful. Mechanical strength measurements of CFRPs using **15** and **19** showed hydroxy groups is more likely to interact with the surface structure of carbon fibers.