

SHORT COMMUNICATION

Novel Bio-Based Polyesters Derived from Curcumin
as an Inherent Natural Diol Monomer

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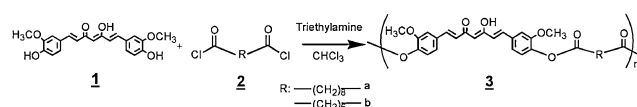
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Design of bio-based plastics derived from renewable resources is one of key technologies to attain sustainable development of modern civilization. In order to reduce the dependency on petroleum resources in chemical industry, a great deal of efforts have been paid to utilize a wide variety of bio-resources. These days, bio-based polymers¹ are of particularly strong interest because the use of such material is believed to lead to reduction of carbon dioxide emission.

In the present paper, we wish to report synthesis of novel polyesters using curcumin as a monomer. Curcumin [5-hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)-1,4,6-heptatrien-3-one]² is well known as yellow coloring dye that is naturally abundant in *Turmeric plant* (*Curcuma longa*). *Turmeric plant* is indigenous to tropical Asia such as India and Malaysia. For many centuries, turmeric has been commonly used as spice (curry) in various foods or medicine for diseases such as inflammatory.³ However, in spite of a great deal of concern toward curcumin and common availability of this compound, it is amazing that it has scarcely been utilized as a bio-resource for material synthesis. From a standing point of polymer synthesis, curcumin has a symmetrical structure and possesses two hydroxyl groups which are available as polymerizable functional group. Therefore, curcumin can be regarded as an inherent natural monomer which can be readily polymerized by conventional polymerization methods. In the field of polymer synthesis, curcumin has been examined as a photoinitiator for polymerization of styrene and methyl methacrylate.⁴ However, there had not been examples of polymer synthesis using curcumin as a monomer itself. Herein, we have prepared novel polyesters bearing β -diketone units in their main chain.

To begin with, a polycondensation of curcumin (**1**) with sebacoyl chloride (**2a**) was examined in chloroform as depicted in Scheme 1. Curcumin was purchased from Tokyo Chemical Industry Co. Ltd. (TCI) and used after recrystallization in 2-propanol. The polymerization was carried out by adding a chloroform solution of sebacoyl chloride to a suspension of an equimolar amount of curcumin in chloroform in the presence of triethylamine at 0 °C. Then, the resulting mixture was stirred for 1 h at room temperature. Although curcumin is poorly soluble in chloroform, the reaction mixture gradually became homogeneous during the polymerization. Some insoluble precipitate was formed when molecular weight of the resulting polymer was large. The insoluble part was removed by filtration before further purification. The obtained crude polymer was reprecipitated in *n*-hexane twice and then obtained polymer was dissolved in chloroform and washed with water three times. After removal of the solvent, yellow-orange colored polymer was obtained in good efficiency. The obtained polyester **3a** was soluble in common organic solvents such as dichloromethane and chloroform. After casting the chloroform solution of the polyester on a glass plate, a yellowish transparent film was readily obtained.

Synthesis of polyester was carried out under various reaction conditions. The results are listed in Table I. In toluene or chlorobenzene, polymerization was not observed possibly due to poor solubility of curcumin monomer. On the other hand, polyesters were efficiently obtained in chloroform. The molecular weights of polymers were estimated from

Scheme 1. Synthetic scheme for polymerization between **1** and **2**.Table I. Polymerization between **1** and **2a** under various reaction conditions^a

Run	Solvent	Conc. ^b (M)	M_n^c	M_w/M_n^c	Yield ^d (%)
1	CH ₂ Cl ₂	0.13	6100	3.62	68
2	toluene	0.13	— ^e	— ^e	— ^e
3	C ₆ H ₅ Cl	0.13	— ^e	— ^e	— ^e
4	CHCl ₃	0.10	21000	2.48	45
5	CHCl ₃	0.13	32000	2.48	68
6	CHCl ₃	0.15	16000	2.31	61
7	CHCl ₃	0.22	14000	2.38	63
8	CHCl ₃	0.40	5000	2.10	64

^aThe reactions were carried out under a nitrogen atmosphere at 0 °C in the presence of 2.0 eq. of triethylamine. ^bConcentration of **1**. ^cEstimated by gel permeation chromatography (CHCl₃ as an eluent, PSt standards).

^dAfter reprecipitation into *n*-hexane twice. ^eNo polymerization.

GPC (gel permeation chromatography) measurement to be in the range of 32000 to 5000. The M_n of the polymer increased with increasing the concentration of both monomers, however, M_n began to decrease at monomer concentration of over 0.13 M because of insufficient solubility of monomers and polymer.

A polycondensation of curcumin with suberoyl chloride (**2b**) was also carried out to afford the corresponding polyester **3b** in 60% yield. The M_n of the obtained polyester was 21000 (M_w/M_n 2.24). On the contrary, when fumaryl chloride or malonyl chloride was employed as a monomer, polymerization was not successful possibly because of lower solubility of oligomers.

The structures of the polymers were supported by ¹H NMR, ¹³C NMR and UV-vis absorption spectra. In the ¹H NMR spectrum of **3a** (Figure 1(a)), the observed peaks and integral ratios were in good agreement with those for expected structure. From the appearance of the peak due to methyne proton of enol structure at 5.84 ppm, it was indicated that β -diketone unit of the polyester **3a** was exclusively in enol form in chloroform solution. The ¹³C NMR spectrum of **3a** (Figure 1(b)) also showed the peak corresponding to methyne carbon of enol structure at 101.8 ppm, while peak due to methylene carbon of β -diketone was not observed. The UV-vis absorption spectrum of **3a** showed a main absorption peak at 400 nm which corresponds to curcumin unit. This also indicates that curcumin structure is retained in the polymer structure.

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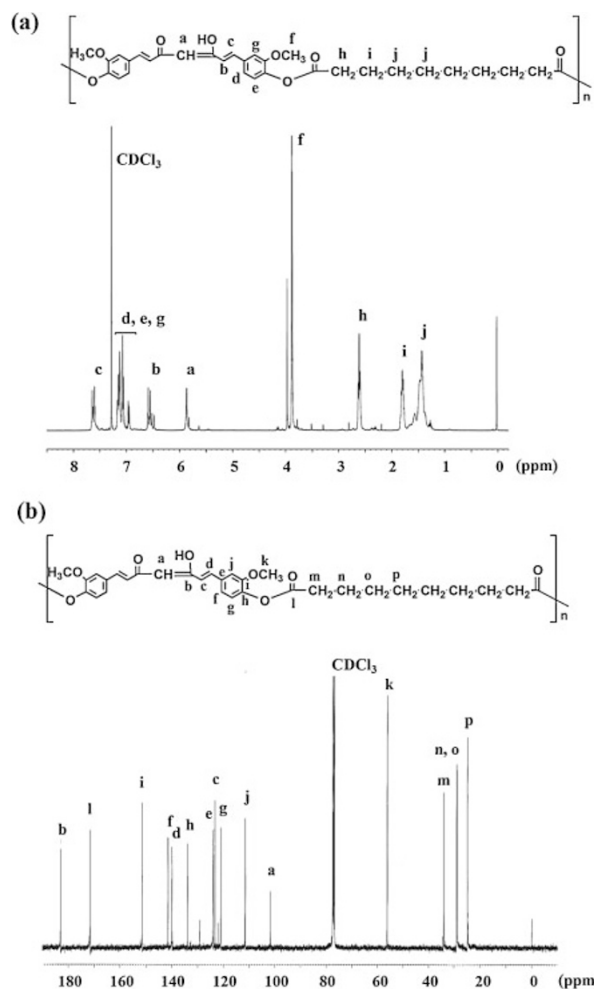
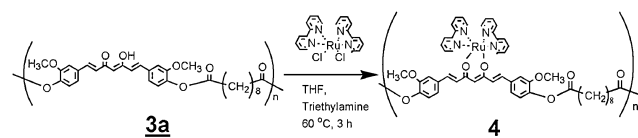


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra for polyester **3a** (in CDCl_3).

In the present system, the polymers obtained are also expected as polymer ligands that are capable of forming a variety of β -diketonate complexes with metal ions. So far, there has been a number of researches on the preparation of polymers with β -diketonate metal complexes⁵ exhibiting light emitting properties, liquid crystalline properties, hole transporting properties. Hence, these polymers obtained should be valuable building block for a variety of functional polymer-metal complexes. As a synthetic method for polymers with β -diketone units, incorporation of β -diketone into the side chain of polystyrene has been examined.^{5b} In the present approach, inefficient preparation of β -diketone unit is not required, therefore, the present method using curcumin would be industrially more beneficial approach.



Scheme 2. Synthetic scheme for the preparation of polyester-ruthenium complex **4**.

Here, as an example of such polymer complex, polyester-ruthenium complex was prepared by reacting the polyester with bis(bipyridyl)dichlororuthenium $[(\text{bpy})_2\text{RuCl}_2]$ ⁶ in tetrahydrofuran in the presence of triethylamine (Scheme 2). After crude polymer solution in chloroform was washed with water, reprecipitation into *n*-hexane afforded a red solid. In the ^1H NMR spectrum of the polymer complex, peaks due to bipyridyl group were slightly shifted to lower field region in comparison with the chemical shifts for $(\text{bpy})_2\text{RuCl}_2$. From the integration ratio of the peaks, it was estimated that ruthenium complex was incorporated in 8.2 unit% of repeating units. The complex formation was also implied in UV-vis absorption spectrum of polymer complex **4**, in which characteristic absorption due to MLCT was observed around 550 nm.

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