

Synthesis of a star-shaped polymer having tris (β -diketonato)chromium(III) at the center core

Kensuke Naka*, Gen-ichi Konishi, Kazuhiro Kotera, Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received: 1 June 1998/Accepted: 9 July 1998

Summary

The metal-centered star-shaped polymer was prepared by coordination of *p*-(1,3-butanedionyl)-terminated poly(oxyethylene) with Cr(III) ion. The structure was confirmed by GPC analysis and IR spectra. The resulting polymer complex was well-soluble in various organic solvents and water.

Introduction

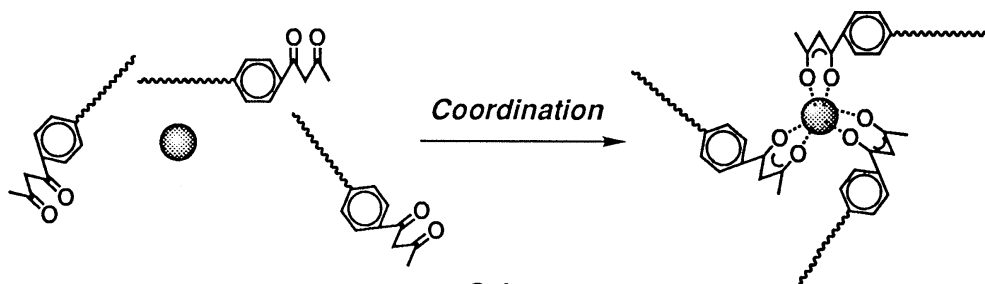
Star-shaped polymer, a kind of branched polymer having more than three linear polymeric arms attached to the center core, has been extensively investigated in a few decades [1-10]. Comparing to a linear polymer, the characteristic properties of these polymers derived from their unique shape were observed in solution or in bulk from various viewpoints.

Recently, we reported the preparation of metal-centered star-shaped polymers by coordination of 2,2'-bipyridyl- [11] or pyridyl-terminated [12] poly(oxyethylene) with Ru(II) ion. Metal-centered star-shaped polymers can be constructed by infinite combinations of both inorganic (metal complex center core) and organic (polymer branches) moieties and have considerable potentials such as electronic, magnetic, photochemical properties. They are also expected to be developed for film-formation and polymer blends. Therefore, they are distinguished from a low molecular weight metal complex from a lot of viewpoints. However, only few attempts have been made at metal-centered star-shaped polymers except for combinations between two or three kinds of transition metals and N-donor ligands [11-13]. It is very important to extend their scope toward other chelates chemistry.

Metal- β -diketone complexes have fruitful potentials in a wide region of chemistry. A large number of transition metal- β -diketone complexes were synthesized [14] and their application for analytical chemistry, Lewis acid catalysts [15] and oxidation catalysts [16]. They also exhibit interesting photochemical behavior [17]. Particularly, tris(β -diketonato)chromium(III) are very stable for acid and ligand exchange reaction. Many studies on electrophilic substitution at methine proton of their complex were reported [18]. Various substituted metal- β -diketone complexes [18-20] and the coordination polymers [21] were prepared by using this principle. This electronic substitution may be derived from their "aromatic character" in the chelate ring [18].

In this paper, we report the preparation of a novel metal-centered star-shaped polymer by coordination of a β -diketone-terminated organic polymer with chromium(III) ion. (**Scheme 1**)

* Corresponding author

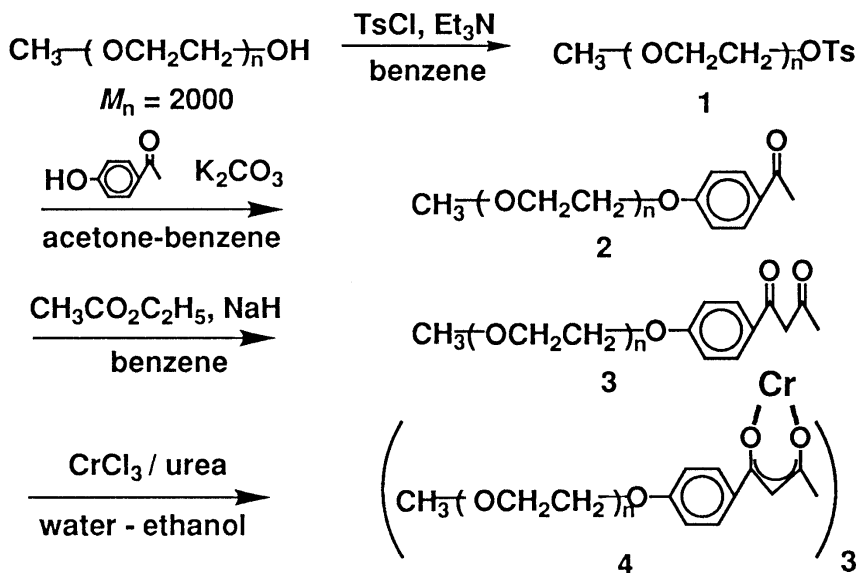


Scheme 1

Results and discussion

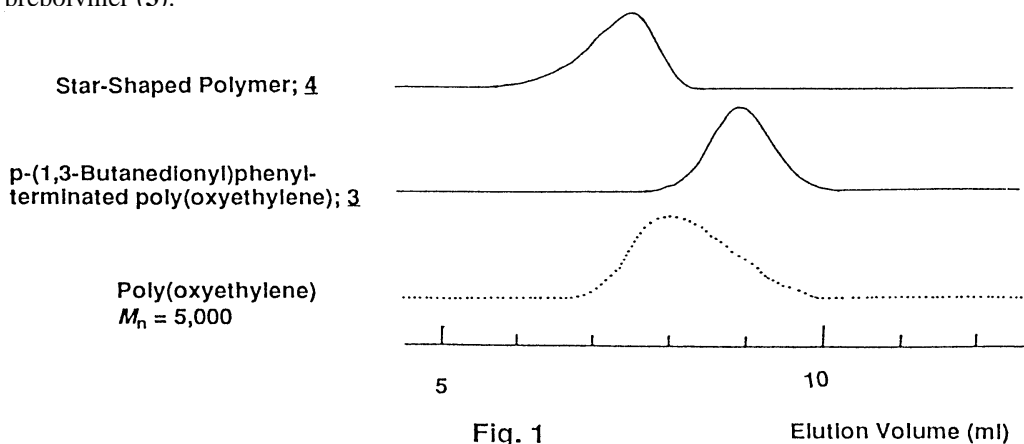
p-(1,3-Butanedionyl)phenyl-terminated poly(oxyethylene) (**3**) was prepared from commercially available poly(oxyethylene) monomethyl ether ($M_n = 2,000$) according to **Scheme 2**. *p*-Acetylphenyl-terminated poly(oxyethylene) (**2**) was obtained by Williamson ether synthesis of tosyl poly(oxyethylene) monomethyl ether (**1**) and *p*-hydroxyacetophenone. After **2** was reacted with ethyl acetate, the product was isolated by reprecipitation from dichloromethane solution into diethyl ether. Although the isolated product (**3**) contained 34 % of **2** determined from $^1\text{H-NMR}$ analysis, we used **3** without further purification for preparation of a star-shaped polymer.

A star-shaped polymer (**4**) was prepared by coordination of **3** with chromium(III) ion. A water-ethanol solution containing an excess amount of **3** with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of urea was stirred under reflux condition for 3 days. After the solvent was removed under reduced pressure, the residue was dissolved in dichloromethane. After filtration, the resulting solution was poured into diethyl ether, and a solid was obtained. This solid was dissolved in water-ethanol solution and the separation of **4** from the remained **2** and **3** was carried out by Advantec Ultrafilter USY-1 (molecular cut-off, 10,000). The brown color product (**4**) was obtained in 48% yield. (**Scheme 2**)



Scheme 2

The GPC measurement for **4** is demonstrated in **Fig 1**. The unimodal peak of **4** was found to be shifted to a high molecular weight region than that of the starting prepolymer (**3**).



The IR spectrum of **3** showed strong absorption at 1602 cm^{-1} due to a mixture of C=O and C=C vibrations. As a model complex, tris(1-phenyl-1,3-butanedionato) chromium(III) shows the metal coordinated C=O vibration band at 1545 and 1510 cm^{-1} [20]. The star-shaped polymer (**4**) showed absorption at 1543 and 1507 cm^{-1} that are assigned to metal coordinated C=O vibrations. This result indicated a formation of tris(β -diketonato)chromium(III) in **4**. The peak of **4** in GPC was shifted to a higher molecular weight region than that of poly(oxyethylene) ($M_n = 5,000$). This observation also supported a formation of tris(β -diketonato)chromium(III).

4 was well-soluble in chloroform, benzene, methanol, THF, and water, but insoluble in hexane and diethyl ether. The solubility of **4** was similar to that of poly(oxyethylene). It is noted that low molecular weight metal- β -diketone complexes are usually soluble in distinct organic solvents and insoluble in water.

The present star-shaped polymer showed film-forming properties, and is expected as a novel photochemical device. Various types of star-shaped polymers can be prepared by coordination of **3** with different transition metals. The research in this direction is in progress in our laboratory.

Experimental section

Materials and instruments

Unless otherwise noted, all materials were obtained from commercial suppliers and used without purification. Preparation of tosyl poly(oxyethylene) monomethyl ether (**1**) was described in the literature [11]. Benzene was distilled from sodium benzophenone ketyl. Acetone was distilled from potassium dicarbonate. $^1\text{H-NMR}$ spectra were recorded at 270 MHz on a JEOL EX-270 in CDCl_3 solution with tetramethylsilane as an internal standard. GPC analysis was carried out on a Shodex K803 by using chloroform as an eluent. IR spectra were recorded by a Perkin-Elmer 1600 FT-IR spectrometer.

p-Acetylphenyl-terminated poly(oxyethylene) (**2**)

1 (8.6 g, 4 mmol) was dissolved in a solution made from each 100 mL of acetone and benzene, potassium dicarbonate (2.7 g, 20 mmol), and *p*-hydroxyacetophenone (5.4 g, 50 mmol). The resulting mixture was refluxed for 36 h. After cooling at room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was dissolved in dichloromethane and reprecipitated in diethyl ether repeatedly to remove *p*-

hydroxyacetophenone. The obtained solid was dried under vacuum and used without further purification. The crude product (**2**, 7.2 g, 84%) was obtained.

p-(1,3-Butanedionyl)phenyl-terminated poly(oxyethylene) (**3**)

A mixture of sodium hydride (60% in an oil dispersion) (500 mg, 12 mmol) and 50 mL of dry benzene was stirred vigorously under nitrogen atmosphere. Then **2** (5 g, 2.4 mmol) and ethyl acetate (2.1 g, 24 mmol) in 50 mL of benzene were added to this solution slowly. The resulting mixture was refluxed for 3 days. After cooling at room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was dissolved in dichloromethane, and reprecipitated in diethyl ether repeatedly. The solid was dried under vacuum and used without further purification. The mixture of **2** and **3** (4.2 g) was obtained. From ¹H-NMR analysis, the degree of acylation was found to be 66%. ¹H-NMR (selected data for **3**) (CDCl₃): δ = 2.17 (s, CH₃, 3H), 3.55-3.91 (m, CH₂, poly(oxyethylene)), 6.11 (s, 1H, enol form), 6.94 (d, *J* = 8.8, 2H, Ar), 7.86 (d, *J* = 8.9, 2H, Ar); IR (KBr): 1602 (ν_{C=O}), 2878 (ν_{C-H}) (cm⁻¹).

Preparation of the star-shaped polymer (**4**)

A mixture of CrCl₃·6H₂O (10.4 mg, 0.039 mmol), the starting prepolymer (**3**) (500 mg, 0.23 mmol of **3**) and 20 mL each of water and ethanol in the presence of urea (250 mg) was refluxed for 3 days. After the reaction mixture was cooled and concentrated under reduced pressure, the polymer part was extracted with 200 mL of chloroform. Removal of solvent under reduced pressure afforded a residue which was dissolved in 30 % of ethanol, and filtered by Advantec Ultrafilter USY-1. The residue was extracted with ethanol, concentrated, and dried under high vacuum. The star-shaped polymer (**4**) was obtained (121 mg, 48%). IR (KBr): 1507 (ν_{C=O}), 1543 (ν_{C=O}), 1598 (ν_{C-C, arom.}), 2879 (ν_{C-H}) (cm⁻¹).

References

- 1 Eschwey H, Burchard W (1975) *Polymer* 16:180
- 2 Bazan GC, Schrock RR (1991) *Macromolecules* 24:817
- 3 Kanaoka K, Sawamoto M, Higashimura T (1991) *Macromolecules* 24:2309
- 4 Toporowski PM, Roovers J, (1986) *J Polym Sci Poly Chem Ed* 24:1986
- 5 Tezuka Y, Goethals EJ (1987) *Makromol Chem* 188:791
- 6 Fujimoto T, Tani S, Takano K, Ogawa M, Nagasawa M (1978) *Macromolecules* 11:673
- 7 Sogah DY, Hertler WR, Webster OW, Gordon MC (1987) *Macromolecules* 20:1473
- 8 Tsukahara Y, Mizuno K, Segawa A, Yamashita Y (1989) *Macromolecules* 22:1546
- 9 Lutz P, Rempp P (1989) *Makromol Chem* 198:1051
- 10 Char X, Zhang X, Shen J (1991) *Macromolecules* 24:4985 (1991)
- 11 Chujo Y, Naka A, Krämer M, Sada K, Saegusa T (1995) *J Macromol Sci-Pure Appl Chem* A32:1213
- 12 Naka K, Kobayashi A, Chujo Y (1997) *Macromol Rapid Commun* 18:1025
- 13 Lamba JJS, Fraser CL (1997) *J Am Chem Soc* 119:1801
- 14 Siedle AR, in *Comprehensive Coordination Chemistry*, ed by Wilkinson G, Pergamon Press (1987) 2:365
- 15 Hay RW, *ibid* 6:411.
- 16 Mukaiyama T, Yamada T (1995) *Bull Chem Soc Jpn* 68:17
- 17 Lewis FD, Miller AM, Salvi GP (1995) *Inorg Chem* 34:3173
- 18 Collman JP (1965) *Angew Chem Int Ed Engl* 4:132
- 19 Reihlen H, Illig R, Wittig R (1925) *Chem Ber* 55B:12
- 20 Collman JP, Moss RA, Maltz H, Heindel CC (1961) *J Am Chem Soc* 83:531
- 21 Archer RD, Lauterbach A, Ochaya VO (1994) *Polyhedron* 13:2043