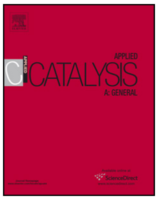
Applied Catalysis A: General 464–465 (2013) 51–60

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Influence of method of preparation of solid, double-metal cyanide complexes on their catalytic activity for synthesis of hyperbranched polymers

Joby Sebastian, Darbha Srinivas*

Catalysis Division, National Chemical Laboratory, Pune 411 008, India

ARTICLE INFO

Article history:
Received 18 February 2013
Received in revised form 7 May 2013
Accepted 19 May 2013
Available online 25 May 2013

Keywords:
Double-metal cyanide
Hydrophobic solid acid catalyst
Heterogeneous catalysis
Dendrimers
Hyperbranched polymers

ABSTRACT

Catalytic activity of a series of Fe–Zn double-metal cyanide (DMC) complexes with varying structural and acidic properties has been investigated for the synthesis of hyperbranched polyesters (HPs) from glycerol and succinic acid/adipic acid. The DMC complexes were prepared using different complexing and co-complexing agents. Hydrophobicity of the surface, Lewis acidity and micro–mesoporous architecture are the critical features of DMC enabled control on gelation process in preparing HPs of high degree of branching. The micro–mesoporous architecture of DMC acts as a nano-reactor for reactant molecules to form primary condensation products which further polymerize yielding dendrimers. Hyperbranched polyesters of degree of branching as high as 90% could be achieved without gelation using DMC catalysts.

1. Introduction

Hyperbranched polymers (HPs) are randomly branched polymeric architectures belonging to the major class of dendritics [1]. While dendrimers are three-dimensional, highly symmetric structures with degree of branching (DB) of 100%, HPs are three-dimensional, asymmetric structures with DB in the range 40–60%. Though, both these polymers are structurally different from each other, their chemical properties like viscosity, solubility, reactivity and functional groups are similar. Due to the tedious synthesis procedures of dendrimers involving protection, deprotection and chromatographic separation as compared to the simple synthetic procedures, purification by precipitation and scaling-up opportunities of HPs, the latter have been gaining greater importance [1]. Topological specifics of HPs like, high level of solubility and compatibility, low viscosity of solutions, resistance to aggregate even in concentrated solutions, ability to function as nano containers for substances sorbed inside, weak dependence of hydrodynamic volume on molecular weight and lump of free ends of chains with functional groups on their periphery open a new window for their diverse industrial applications. HPs find wide application in cosmetics, food additives, surfactants, lubricants, plasticizers, drug delivery agents, azeotropic phase separators, orthopaedic and ophthalmic fields, additives in paints, adhesive promoters, sealants, and casting elastomers, and as rheology modifiers and surface or interface modifiers [2,3]. Discovery of unique properties of hyperbranched polyesters has expedited a rapid development in this area of materials. Hyperbranched polyesters derived from renewables broaden their applicability as novel, environmentally-friendly materials for various applications.

Glycerol is widely available and is rich in functionalities. Its effective utilization is a key factor that can facilitate the economically-viable production of biodiesel at commercial scales. For every 9 tons of biodiesel produced, about 1 ton of glycerol is formed as by-product [4]. Since glycerol carries three —OH functionalities required enough to form branching segments, it opens up a viable possibility for the synthesis of biodegradable polymers. Polyesterification of glycerol (G) with biomass-derived dicarboxylic acids viz., succinic acid (SA) and adipic acid (AA), producing HPs will, thus, speak about a sustainable process and a meaningful way for glycerol utilization and value-addition.

Several homogeneous catalyst systems including mineral acids and dibutyl tin have been reported for this process [5,6]. Recovery/reuse, air/moisture sensitivity and corrosion of the reactor/pipe lining are some of the serious issues with these homogeneous catalyst processes [7,8]. Further, the polyesters prepared using dibutyl tin catalysts have a DB of only 48% [5]. Use of aprotic solvent to control gelation process and to increase DB is far from satisfaction [6]. The product oligomer was found difficult to separate from the reaction medium as the solvent, dimethyl formamide reacted with the acid terminals of the branched oligomers [6]. Enzymes catalyse this reaction at ambient conditions, but require longer

---

* Corresponding author. Tel.: +91 20 2590 2018; fax: +91 20 2590 2633.
E-mail address: d.srinivas@ncl.res.in (D. Srinivas).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.05.024

Table 1
Fe–Zn DMC catalysts, their designation, physicochemical properties and catalytic activity data.

Catalyst	Reagents used in catalyst synthesis		Structural properties			Total acidity (mmol/g; NH_3-TPD)	Catalytic activity[d]		
	Complexing agent	Co-complexing agent	Inter planar spacing (d_{200}; nm)	Unit cell parameter (a; nm)	Crystallite size (nm)[c]		Isolated yield of polyester (wt%)	Degree of branching (DB; mol%)[e]	Inherent viscosity (η; dl/g)[f]
DMC-0	–	–	0.448	0.900	51.2	3.52	53.8	49.5	0.039
DMC-1	*tert*-Butanol	PEG-300	0.448	0.896	52.8	3.87	52.3	43.8	0.048
DMC-2	*tert*-Butanol	PEG-600	0.449	0.898	49.6	4.82	63.4	48.8	0.038
DMC-3	*tert*-Butanol	PEG-1500	0.449	0.899	47.5	5.30	66.2	50.3	0.033
DMC-4	*tert*-Butanol	PEG-4000	0.450	0.900	43.6	7.10	76.2	55.9	0.037
DMC-5[a]	*tert*-Butanol	PEG-4000	0.448	0.896	33.7	8.23	75.7	44.6	0.044
DMC-6[b]	*tert*-Butanol	PEG-4000	0.450	0.900	59.5	3.14	70.6	42.0	0.045
DMC-7	Methanol	PEG-4000	0.449	0.899	55.2	3.30	71.5	43.2	0.064
DMC-8	Glycerol	PEG-4000	0.449	0.894	57.5	4.28	71.4	45.0	0.044

[a] In the preparation of DMC-5 (see Section 2.1), solutions 2 and 3 were mixed first and added to solution 1.

[b] In the preparation of DMC-6, solutions 1 and 3 were mixed first and solution 2 was added to this mixture.

[c] Determined using the Debye–Scherrer formula.

[d] Reaction conditions: succinic acid (SA) = 1.773 g, glycerol (G) = 0.935 g, glycerol:SA (functional groups molar ratio) = 1:1, catalyst = 0.08 g (i.e., 3 wt% of total reactants), reaction temperature = 180 °C, reaction time = 1.5 h.

[e] Estimated from inverse-gated and DEPT ^{13}C NMR spectral measurements of the product G-SA hyperbranched polyester.

[f] Values at 29 °C using tetrahydrofuran (THF) as solvent.

reaction times (>48 h) [9]. Controlled gelation at high conversions is an issue in these processes. Tuning the topological characteristics of hyperbranched polyesters is desirable to focus their application in specialized fields. A solid catalyst-based process has several engineering, environmental and economic advantages [10]. The solid catalyst can be easily separated and reused in subsequent recycles. In a recent communication, we demonstrated that Fe–Zn double-metal cyanide (DMC) is an efficient and reusable, solid acid catalyst for producing glycerol-succinic acid (G-SA) and glycerol-adipic acid (G-AA) hyperbranched polyesters [11]. DMC has been known as a catalyst for preparing polyether polyols [12–16], alternative copolymerization of epoxides and CO_2 [17–22], β-amino alcohols [23] and transesterification [24,25]. Hydroamination [26,27] and Prins condensation reactions [28]. We extended their application for the synthesis of hyperbranched polyesters [11]. G-SA and G-AA polyesters with high DB at controlled gelation and high conversion of glycerol were obtained over DMC catalyst. As an extension to our earlier communication, we report here, the influence of method of preparation of DMC on its catalytic activity in the synthesis of hyperbranched polyesters. Method of preparation can alter the structural and acidic properties of the catalyst. DMC is known to exhibit micro–mesoporous architecture [11]. While enabling facile diffusion of reactant molecules, these micro–mesopores act as nano reactors controlling DB of hyperbranched polyesters formed in the synthesis.

2. Experimental

2.1. Catalyst preparation

DMC is known to be prepared in the presence of complexing and co-complexing agents [25]. In this study, we have used methanol, *tert*-butanol and glycerol as complexing agents. Polyethylene glycols of varying molecular weight (PEG-300, PEG-600, PEG-1500 and PEG-4000) were used as co-complexing agents. We have also changed the mode of addition of metal salt precursors and prepared different DMC catalysts.

DMC-1 was prepared using *tert*-butanol as a complexing agent and PEG-300 as a co-complexing agent. In a typical preparation of DMC-1, solution 1 was made by dissolving 0.01 mol of $K_4[Fe(CN)_6]$ (Merck, India) in 40 ml of double-distilled water. Solution 2 was prepared by dissolving 0.1 g of $ZnCl_2$ (Merck, India) in a mixture of distilled water (100 ml) and *tert*-butanol (20 ml). PEG-300 (15 g) was separately dissolved in 2 ml of distilled water and 40 ml of *tert*-butanol to prepare solution 3. Solution 2 was added slowly to solution 1 at 50 °C over 1 h with vigorous stirring. White precipitation occurred during the addition. Then, solution 3 was added to the above reaction suspension over a period of 5 min and stirring was continued for another 1 h. The solid cake formed was filtered, washed with 500 ml of distilled water, and dried at 25 °C for 2–3 days. This material was activated at 180–200 °C for 4 h prior to using in the reactions and in characterization studies.

DMC-2, DMC-3 and DMC-4 were prepared as described above but using PEG-600, PEG-1500 and PEG-4000, respectively, as co-complexing agent. In the preparation of DMC-7 and DMC-8, methanol and glycerol, respectively, were used as complexing agents; PEG-4000 was used as a co-complexing agent.

The preparation of DMC-5 was same as that of DMC-4, except solutions 2 and 3 were mixed first and then, added to solution 1. In the preparation of DMC-6, solutions 1 and 3 were mixed first and solution 2 was added to that mixture.

For comparison, DMC-0 was prepared without using any complexing and co-complexing agent. Table 1 lists the designation of different DMC catalysts prepared in this work.

2.2. Reaction procedure

The polymerization reactions were carried out in a glass, double-necked, round-bottom flask placed in a temperature-controlled oil bath. No solvent was used during the polymerization step. Known quantities of diacid (succinic acid – SA or adipic acid – AA) and glycerol were added to the reactor. The contents were flushed with dry nitrogen. Then, DMC catalyst (3 wt% of total reactants) was added. Temperature was raised to 160–180 °C and the reaction was conducted for 1–2 h while stirring the contents vigorously using a magnetic stirrer and flushing with dry nitrogen gas. At the end, the contents were dissolved in acetone. The polymeric product and any left out starting material (glycerol and/or diacid) were completely miscible with acetone and went into the liquid portion. The solid catalyst remained as a separate phase which was removed easily by centrifugation (8000 rpm for 10 min)/filtration from the liquid portion. Then, the polymer product was reprecipitated from the liquid portion by adding n-heptane. Reactants remained in acetone-heptane mixture. Product HP was subjected to characterization. The polymeric product was completely free from any catalyst contaminants.