



Preparation, curing kinetics, and properties of a novel low-volatile starlike aliphatic-polyamine curing agent for epoxy resins

Jintao Wan^{a,b}, Zhi-Yang Bu^a, Cun-Jin Xu^{a,c}, Bo-Geng Li^{a,*}, Hong Fan^{a,**}

^a State Key Laboratory of Chemical Engineering, Department of Chemical and Biochemical Engineering, Zhejiang University, Hangzhou 310027, China

^b Zhejiang Jiamin Plastics Co. Ltd., Jiaying 314027, China

^c College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China

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ABSTRACT

A novel low-volatile starlike aliphatic polyamine with extraordinarily high $-NH_2$ functionalities, N,N,N',N'-penta(3-aminopropyl)-diethylenetriamine (PADT), is synthesized and its molecular structure is confirmed by the FTIR, 1H NMR and ESI-MS analysis. Then PADT is employed as the curing agent for the epoxy resin of diglycidyl ether of bisphenol A (DGEBA) and the isothermal reaction of DGEBA/PADT is systematically investigated with differential scanning calorimetry (DSC) according to the model-fitting approach and model-free advanced isoconversional method developed by Vyazovkin. The result shows that PADT possesses the high reactivity and the reaction is autocatalytic in nature. The further reaction kinetic analysis indicates that the Kamal model can well fit the reaction rate at the reaction-controlled stage, whereas the extended Kamal model with a diffusion term can provide an excellent match throughout the isothermal reaction. On the other hand, the model-free kinetic analysis reveals a strong dependence of effective activation energy, E_{α} , on fractional conversion, α , which could mirror the drastic change of the reaction mechanisms, in particular, the rapid drop in E_{α} observed in the deep-conversion regime due to the diffusion-controlled reaction kinetics. Then, a dynamic mechanical analysis (DMA) of the cured DGEBA/PADT network discloses three relaxations from the low- to high-temperature range: β ($T_{\beta} = -34.4^{\circ}C$), α' ($T_{\alpha'} = 68.0^{\circ}C$) and α ($T_{\alpha} = 144.3^{\circ}C$). Moreover, compared to linear propanediamine, PADT can much increase the crosslink density and glass temperature of the cured epoxy resin. Finally, the thermogravimetric (TG) analysis reveals PADT, like propanediamine, can impart the cured epoxy resin with the excellent thermal stability with the initial decomposition temperature as high as $\sim 300^{\circ}C$. On the basis of these experimental data, we can conclude that PADT exhibits a great potential to partially replace conventional high-volatile aliphatic-amine curing agents of low molecular weights.

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1. Introduction

Epoxy resins find a broad spectrum of applications in coatings, adhesives, castings, modeling compounds, impregnation materials, high-performance composites, insulating materials, encapsulating and packaging materials for electronic devices, and so forth [1–5]. Due to their great industrial significance, epoxy resins have long been receiving a lot of scientific and technical interests, especially their curing reactions and structure–property relationships. To achieve well-balanced ultimate properties, uncured epoxy resins must be converted into a crosslinked macromolecule in the presence of different kinds of curing agents under optimal curing and processing conditions. Among frequently used curing agents for epoxy resins, amine-based ones, especially aromatic and aliphatic

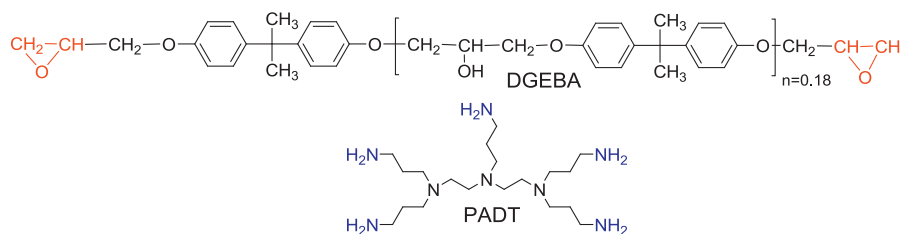
amines, are of prime significance in practical applications. Nowadays, most related scientific work is focused on aromatic-amine curing agents, yet little attention is paid to developing aliphatic-amine ones. Although aromatic-amine curing agents can endow their cured epoxy resins with improved thermomechanical properties and fire resistance, they still suffer from their low reactivity and high melting temperatures. For this reason, high-temperature cure must be applied to improve the compatibility of aromatic-amine curing agents with epoxy resins and to accelerate curing reactions. On the other hand, aliphatic-amine curing agents can well cure epoxy resins at room and even somewhat lower temperatures without heating because they have high reactivity and low melting temperatures, accounting for their principal applications in room-temperature-cure epoxy coatings and adhesives [2].

Traditionally, aliphatic-amine curing agents of low molecular weights have the disadvantages of the strong volatilization, high toxicity, skin irritation and sensitization, fast absorption of carbon dioxide and vapor in air, and strict stoichiometry with respect to epoxy resins [6]. As a result, sometimes they are chemically

* Corresponding author. Tel.: +86 571 87952623; fax: +86 571 87951612.

** Corresponding author. Tel.: +86 571 87957371; fax: +86 571 87951612.

E-mail addresses: bgli@zju.edu.cn (B.-G. Li), hfan@zju.edu.cn (H. Fan).



Scheme 1. Molecular structures of epoxy resin (DGEBA) and curing agent (PADT).

modified to form corresponding amine adducts of increased molecular weights to reduce the unfavorable odor, enhance handling safety, extend stoichiometry, decrease toxicity and improve surface appearance of epoxy resins [2,7]. Unfortunately, such modification will sacrifice some desired properties of epoxy resins such as crosslink density, thermal stability and resistance, processability, reactivity, and mechanical strengths. To this end, recently amine acids (i.e., DL-lysine [8] and L-tryptophan [7]) have been used to cure epoxy resins, which take the advantages of the reduced toxicity and environmental friendliness. These curing agents, however, have the high melting points (i.e., 170 °C (decompose) for DL-lysine and (280–285 °C (decompose) for L-tryptophan found at www.sigmaaldrich.com), which leads to their poor compatibility with and low reactivity towards epoxy resins at room temperature, therefore greatly limiting their potential applications in epoxy formulations, especially, room-temperature-cure epoxy coatings and adhesives.

To meet this challenge, the crux of the problem is to develop new aliphatic-amine curing agents with high reactivity and good compatibility, which needs judicious design of their molecular compositions and topology. Exploring aliphatic-polyamine curing agents with nonlinear architectures [9–13] shows a great promise, since lowered bulk viscosity, decreased tendency to crystallize, and reduced toxicity and irritation can be achieved without much sacrificing other desired good properties, in particular, the high reactivity, good compatibility, and crosslink density of cured epoxy resins.

The major objective of this work is to develop and systematically study a novel nonlinear starlike aliphatic-polyamine curing agent for epoxy resins, N,N,N',N''-penta(3-aminopropyl)-diethylenetriamine (PADT), which quite differs in the molecular topology from common linear aliphatic-amine curing agents. This paper will focus upon the synthesis and characterization of PADT, isothermal reaction, dynamic mechanical properties, and thermal stability of its cured DGEBA system. PADT has high functionalities, low bulk viscosity and very low vapor pressure at room temperature. We shall demonstrate that PADT is highly reactive and can impart its cured epoxy resin with the particularly good thermal properties and significantly increased crosslink density compared to a typical linear aliphatic-amine curing agent (e.g., propanediamine). Especially, this study will afford a deep insight into the isothermal reaction kinetics of DGEBA/PADT by applying the contemporary model-fitting and model-free isoconversional methodologies.

2. Experimental

2.1. Materials

Regent-grade diethylenetriamine and acrylonitrile (Shanghai Reagent Co., Ltd., China) were purified by reduced-pressure distillation prior to use, and propanediamine (99%, Acros Organics) was used as received. DGEBA, diglycidyl ether of bisphenol A, was obtained from Heli Resin Co., Ltd., China with the epoxide equivalent

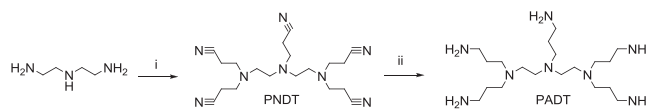
weight (EEW) of 196 g/eq. Raney nickel, the catalysis for hydrogenation, was prepared by dissolving Al in an Al–Ni alloy (w/w = 50/50, Shanghai Reagent Co., Ltd., China) in NaOH–water solution. PADT, see Scheme 1, N,N,N',N'',N'''-penta(3-aminopropyl)-diethylenetriamine, was prepared in our lab, as detailed in Section 2.2. Other chemicals were used directly without purification.

2.2. Synthesis and characterization of PADT

PADT was prepared with reference to the procedures for preparation of poly(propyleneimine) dendrimers [14,15] with a certain modification. As demonstrated in Scheme 2, the synthesis of PADT begins with bimolecular Michael addition [16] between diethylenetriamine and excessive acrylonitrile under ambient conditions to yield a polynitrile intermediate (PNDT), followed by the heterogeneously catalyzed hydrogenation of PNDT to the corresponding polyamine (PADT), as detailed below.

Magnetically stirred diethylenetriamine (60 g) was diluted slowly at room temperature with distilled water (120 g) in a round-bottom flask (500 ml) fitted with a dropping funnel, stirrer and condensation column, and then excessive acrylonitrile (200 g) was added dropwise with continuous stir in 3 h. After that, the reaction mixture was warmed to 40 °C for 1 h and then heated to reflux (about 80 °C) for additional 20 h. Finally, the unreacted acrylonitrile and water were removed with a rotatory evaporator under reduced pressure, and the obtained crude product was recrystallized from ethanol (3 × 800 ml) to afford the nitrile-terminated intermediate, viz. N,N,N',N'',N'''-penta(3-nitrilepropyl)-diethylenetriamine (PNDT), in a good yield (~94%).

Into a high-pressure autoclave (2000 ml), finely powdered PNDT (100 g), ethanol (95%, 1200 ml), Raney nickel (100 g) and solid NaOH (48 g) were charged. After replacing the air by N₂ three times and then by H₂ three times, the H₂ pressure in the autoclave was increased to 20 atm with continuous agitation (800 rpm). As the reaction progressed, the pressure would decrease gradually. Once the pressure fell down to ≤8 atm, recharge it to 20 atm occasionally. The completion of the whole hydrogenation process would spend about 10–12 h, as indicated by no further decrease in the pressure. Subsequently, release the residual pressure, unload the crude product, filter off the unsolvable solid, and concentrate the filtrate, leading to a two-layer liquid product. The upper organic layer was collected and extracted by toluene combined with a small amount of distilled water three times, then concentrated, and further purified using a silica-gel chromatographic column with menthol as the eluent. Removal of the solvent in the collected fraction afforded the targeting liquid compound (PADT) in slightly yellow (~76% yield).



Scheme 2. Synthetic route to N,N,N',N'',N'''-penta(3-aminopropyl)-diethylenetriamine (PADT). i. excessive acrylonitrile, in water, 80 °C for 20 h; ii. Raney nickel, H₂ at 8–20 atm, in ethanol–water (95/5, v/v), room temperature for 10–12 h.

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