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# Acrylonitrile-capped poly(propyleneimine) dendrimer curing agent for epoxy resins: Model-free isoconversional curing kinetics, thermal decomposition and mechanical properties

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## HIGHLIGHTS

- ► We compare the isoconversional curing kinetics of DGEBA/1.0GPPI and DGEBA/PAN4.
- ► Acrylonitrile-capped PAN4 is much lower reactive than controlled 1.0GPPI.
- ► TG analysis shows the two cured epoxy systems are thermally stable up to 200 °C.
- ► DMA results reveal the viscoelastic response of the two cured networks differs greatly.
- ► PAN4 greatly improves the shear, impact strengths and processability of the epoxy.

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## ABSTRACT

Acrylonitrile-modified aliphatic amine adducts are often used as curing agents for room-temperature epoxy formulations (coatings, adhesives, sealants, castings, etc.), yet the curing reaction and properties of resultant epoxy systems still remain less fundamentally understood. Herein we systematically investigate our newly-developed acrylonitrile-modified multifunctional polyamine curing agent for bisphenol A epoxy resin (DGEBA): an acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4). The impact of the molecular structure of PAN4 and a controlled poly(propyleneimine) dendrimer (1.0GPPI) on the curing reactivity, reaction mechanisms, thermal stability, viscoelastic response and mechanical properties of the epoxy systems are highlighted. Differential scanning calorimetry (DSC) confirms DGEBA/PAN4 shows markedly lower reactivity and reaction exotherm than DGEBA/1.0GPPI, and the model-free isoconversional kinetic analysis reveals that DGEBA/PAN4 has the generally lower reaction activation energy. To be quantitative, the progress of the isothermal cure is predicted from the dynamic cure by using the Vyazovkin equation. The isothermal kinetic prediction shows that DGEBA/PAN4 requires about 10 times longer time to achieve the same conversion than DGEBA/1.0GPPI, which agrees with the experimentally observed much longer gel time of DGEBA/PAN4. Subsequently, dynamic mechanical analysis shows that PAN4 results in the cured epoxy network with the lower $\beta$- and glass-relaxation temperatures, crosslink density, relaxation activation energy, enthalpy, entropy, but the higher damping near room temperature than 1.0GPPI. Finally, thermogravimetric analysis (TGA) demonstrates cured DGEBA/PAN4 is thermally stable up to 200 °C, and mechanical property tests substantiate that PAN4 endows the cured epoxy with much higher impact and adhesion strengths than 1.0GPPI. Our data can provide a deeper insight into acrylonitrile-modified aliphatic amine curing agents from the two good model compounds (PAN4 and 1.0GPPI).

## 1. Introduction

Epoxy resins have many attractive properties such as high adhesion strength, dimension stability, low cure shrinkage, excellent chemical and heat resistance, formulation diversity, favorable processability, etc., hence accounting for their extensive

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applications in anticorrosive coatings, composite matrices, potting materials, electronic-packaging molding compounds, structural adhesives, sealants, and so on [1–3]. Uncured epoxy resins are composed of monomers and/or oligomers having two or more reactive epoxy groups, and in practical applications they must be transformed to a highly crosslinked network in the presence of curing agents. The most wildly used epoxy resins holding about 80% market share belong to the bisphenol-A type with different molecular weight ranges. The ultimate bulk properties of epoxy resins depend strongly on properly selecting a properly selected curing agent under optimal curing conditions. In general, epoxy curing agents include amines, acid anhydride, phenolic resins, mercaptans, etc., among which amines are the most important. In particular, aliphatic amines are highly reactive and can cure epoxy resins well even at room temperature, so that they find vast usages in room-temperature epoxy coatings and adhesives.

Nevertheless, conventional aliphatic-amine curing agents have low molecular weights, which leads to their high volatility, strong toxicity, skin sensitization, very strict dosage, "surface flush" resulting from the rapid absorption of carbon dioxide and vapor in air, and so on [4,5]. For this reason, usually low-molecular-weight aliphatic amine curing agents are modified chemically to increase molecular weights and to achieve desired properties such as reduced volatility and toxicity, increased dosage and pot life, improved flexibility, surface appearance and mechanical performances, etc., and they are most frequently modified by acrylonitrile or butyl-glycidylether. On the other hand, recently the use of dendritic aliphatic amino-terminated dendrimers such as poly(propyleneimine) (PPIs) [6–12], polyamidoamine (PAMAMs) [13,14] and poly(ester-amine) (PEAs) [15] as novel curing agents are capturing increasing research interest. These dendrimers have the much high molecular weights combined with extraordinarily high functionalities compared to conventional aliphatic amines, so that they show low volatility and high reactivity. More interestingly, PPIs, consisting only of C–C and C–N linkages, can be used as raw materials to produce novel amine adducts by a suitable chemical modification method [16,17]. These resulting amine adducts may have more sophisticated properties, because PPIs have the high functionalities, reactivity, branched molecular structure, and excellent thermal stability.

For example, in 2011 we reported two kinds of novel amine adduct curing agents for epoxy resins: butylglycidylether-modified poly(propyleneimine) dendrimers (PB2 and PB4) [16] and acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4) [17]. We found that curing reaction of the epoxy systems are greatly affected by the attached butylglycidylether and acrylonitrile moieties of these curing agents. In particular, as demonstrated in Scheme 1, PAN4 has four reactive amino groups with high nitrile group content and precise molecular symmetry. We have established a rate equation to predict the nonisothermal curing rate constant of DGEBA/PAN4. Nevertheless, to date there are lack of the systematic efforts dedicating to the reaction mechanisms, isothermal curing kinetics, and properties of cured DGEBA/PAN4, and especially there remains a need for more comprehensive research to elucidate how the $-CH_2CH_2CN$ substituent on the amino groups of PAN4 affects the curing characteristics, thermal and bear-loading properties of the epoxy system. Such knowledge is important to better design and further guide better applications of acrylonitrile-modified dendritic polyamines curing agents.

In this work, we investigate the model-free isoconversional curing kinetics, dynamic mechanical properties, thermal decomposition, and mechanical properties of DGEBA/PAN4 and DGEBA/1.0GPPI in a systematic and comparative way. We shall elucidate how acrylonitrile-capped PAN4 affects the curing mechanisms, isothermal kinetics, processability, thermal, and dynamic and static mechanical properties of the resulting epoxy systems. Our current contribution will provide the comprehensive data to better understand properties of acrylonitrile-modified aliphatic amine curing agents, which is expected to be helpful for molecular design and further applications of aliphatic amine adduct curing agents.

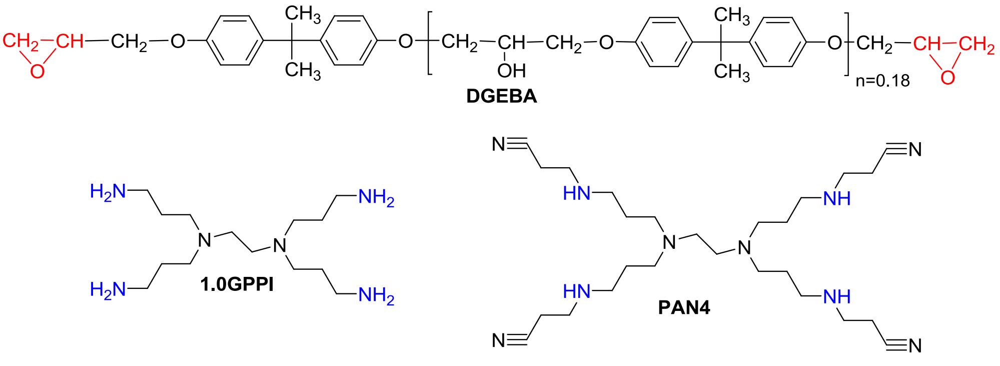
## 2. Experimental

### 2.1. Materials

Ethylenediamine and acrylonitrile were purchased from Shanghai Reagent Co., Ltd., China, and were purified by reduced-pressure distillation. Propanediamine (Acros Organics) was used as received. Diglycidylether of bisphenol-A (DGEBA) (EEW = 196 g/equiv.) was obtained from Heli Resin Co., Ltd., China and dried at 100 °C in vacuum for 1 h before use. N,N,N′,N′-tetra(3-aminopropyl) ethanediamine (1.0GPPI) was prepared from ethylenediamine, acrylonitrile and $H_2$ according to published procedures [18,19]. The acrylonitrile-capped poly(propyleneimine) dendrimer (PAN4, CAS register number: 1267530-15-3) [17] has been synthesized in our laboratory for the first time. The molecular structures of DGEBA, 1.0GPPI and PAN4 are illustrated in Scheme 1.

### 2.2. DSC measurements

The nonisothermal curing reactions of DGEBA/1.0GPPI and DGEBA/PAN4 were followed by a PerkinElemer differential scanning calorimeter (DSC-7). All the DSC experiments were performed under $N_2$ protection, the scanning temperature was from 25 to 250 °C, and the heating rates were 5, 10, 15, and 20 °C min$^{-1}$. The



Scheme 1. Molecular structures of DGEBA, 1.0GPPI and PAN4.