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Synthesis and nonisothermal reaction of a novel acrylonitrile-capped poly(propyleneimine) dendrimer with epoxy resin

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Abstract A novel acrylonitrile-capped poly(propylene imine) dendrimer (PAN4) was synthesized and characterized with FTIR and ^{1}H-NMR. PAN4 and its precursor (poly-(propylene imine) dendrimer (1.0GPPI) were employed to cure bisphenol A epoxy resin (DGEBA), and the nonisothermal reaction kinetics of DGEBA/PAN4 and DGEBA/1.0GPPI was systematically investigated using a differential scanning calorimeter (DSC) in a comparative way. The apparent activation energies determined with the Kissinger method were 59.7 kJ/mol for DGEBA/1.0GPPI and 53.9 kJ/mol for DGEBA/PAN4. Applied the Málek method, it was found that a two-parameter autocatalytic model (SB(m, n)) could well simulate the reaction rates, and further analysis of the reaction rate constants showed PAN4 could cure DGEBA at a greatly decreased rate by a factor a more than ten compared with 1.0GPPI control.

Keywords Epoxy resin · Poly(propyleneimine) dendrimer · Amine-adduct · Curing agent · Nonisothermal reaction kinetics

Introduction

Epoxy resins are extensively used in surface coatings, adhesives, laminating, castings, matrices for advanced composites, electronic encapsulation materials, sealants, etc., due to their vast formulation versatilities, low shrinkage during curing, good chemical resistance, outstanding adhesion, strong mechanical strength, and other desired properties [1–7]. To achieve excellent all-round properties, epoxy resins must convert into a crosslinked three-dimensional polymer in the presence of curing agents via various reaction mechanisms. Furthermore, curing agents play an extremely important role in determining curing schedules, processing, network structures, and end-use properties of epoxy materials [8–12].

Tremendous studies have been performed on the epoxy curing agents in the past decades. The most commonly used include amine, acid anhydride, imidazole, BF_3 complex curing agents, etc., among which the first class is of primary importance, achieving a great variety of technical acceptances in practical applications [13–15]. Amine-based curing agents can be mainly grouped into three subclasses: aliphatic, aromatic, and alicyclic amines, among which the aliphatic amines are able to well cure epoxy resins at room temperature even without post cure, which accounts for their extensive usages in room-temperature coatings, adhesives, and sealants [14]. The conventional low molecular weight elementary aliphatic amines, however, always suffer from their high vapor pressure, strong toxicity, low amine equivalent weight, strict stoichiometry with respect to epoxy resins, and surface flush of their cured epoxy resins arising from easy absorption of carbon dioxide and vapor in air [14, 16]. To settle these problems and to impart epoxy resins with improved specific properties, elementary aliphatic amines are sometimes chemically associated with functional compounds to form derivative amine-adducts, leaving sufficient reactive amine functionalities to crosslink epoxy resins. Although amine-adducts have been widely used as epoxy curing agents for many decades, fundamental research on their properties, particularly the curing

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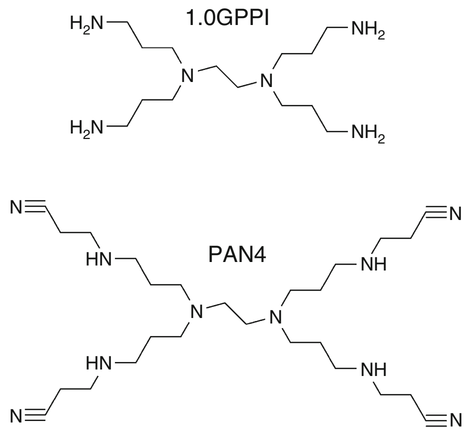
reactions with epoxy resins is extremely rare to date in open literature [17, 18]. On the other hand, technical exploitation of amine-adduct curing agents primarily focuses on chemical modification of polyethylenepolyamines, due largely to the restriction of elementary aliphatic amines available now. To this end, it is very necessary to carry out more fundamental and systematic work on this topic to gain a better understanding of influences of amine-adducts on curing reactions and other properties of resulting epoxy systems, and to develop new amine-adducts to meet a broader range of applications in practical epoxy formulations.

The major objectives of this work are to develop a new amine-adduct as the curing agent for epoxy resins and to acquire a more basic understanding of the reaction of the resultant epoxy systems. Herein, we report an original, systematic work on synthesis and characterization of a novel acrylonitrile-modified aliphatic polyamine (PAN4) with a perfect dendritic molecular architecture, and nonisothermal reaction kinetics of bisphenol A epoxy resin with PAN4 and its precursor (poly(propylene imine) dendrimer (1.0GPPI) as the curing agents.

Experimental

Materials

Ethylene diamine and acrylonitrile were purchased from Shanghai Reagent Co., Ltd., China and purified by distillation under reduced pressure before use. DGEBA, diglycidylether of bisphenol A (EEW = 196 g/equiv.), was obtained from Heli Resin Co., Ltd., China (EEW = 196 g/equiv.). 1.0GPPI (Scheme 1), *N*,*N*,*N*′,*N*′-tetra(3-aminopropyl) ethanediamine (1.0GPPI) was synthesized according to the procedures described in literature [19, 20] with a slight alteration.



Scheme 1 Molecular structures of 1.0GPPI and PAN4

Synthesis of PAN4

Acrylonitrile-capped poly(propylene imine) dendrimer was synthesized via the single-molecule Michael addition between primary amine functionalities and double bonds of acrylonitrile under ambient conditions to afford an amine-acrylonitrile adduct (PAN4); see Scheme 1. To illustrate, synthesis of PAN4 began with adding dropwise acrylonitrile (acrylonitrile:1.0GPPI = 4:1 mol/mol) to magnetically stirred 1.0GPPI in a water batch at 25 °C for 2 h under nitrogen protection, then heated the reaction mixture to 40 °C, and held for another 20 h. Finally, upload the reaction mixture with final product (PAN4) of slight yellow oil obtained.

Instrumentation and characterization

FITR spectra of 1.0GPPI and PAN4 on KBr pallets were conducted on a Nicolet^{TM} 5700 spectrometer with wavenumber ranging from 4000 to 400 cm^{-1}. ^{1}H-NMR spectra of 1.0GPPI and PAN4 were recorded on a Bruck Avance nuclear magnetic resonance spectrometer (400 MHz) with $CDCl_3$ as the solvent and TMS as the internal standard. Heat flows as a function of temperature and time for nonisothermal reactions of DGEBA/1.0GPPI and DGEBA/PAN4 were registered with a Perkin Elemer differential scanning calorimeter (DSC-7) which was previously calibrated with high-pure indium before any measurements. Heating rates were 5, 10, 15, and 20 °C/min with temperature ranging from 25 to 250 °C, and protection gas was dynamic dry nitrogen (20 mL/min). DGEBA and PAN4 or 1.0GPPI were quickly mixed well in stoichiometric ratio at room temperature, and then about 8–10 mg of the fresh mixture was sealed in an aluminum DSC pan, and immediately subjected to a dynamic temperature scan with an identical pan as the reference.

Results and discussion

FTIR and ^{1}H-NMR analyses

FTIR spectra of 1.0GPPI and PAN4 are presented in Fig. 1 where the characteristic absorption bands are marked by broken lines. The primary amine functionalities (–NH_2) of 1.0GPPI can be confirmed by two characteristic bands: the double absorption peaks locating in the wavenumber of 3350–3250 cm^{-1} which corresponds to the stretch vibration of –NH_2 functionalities and another appearing around 1547 cm^{-1} which is attributable to the scissor bending of –NH_2 groups. In contrast, for PAN4 the absorption peaks around 3300 cm^{-1} shrink notably, and that for 1574 cm^{-1} almost completely disappears, whereas a new peak appears

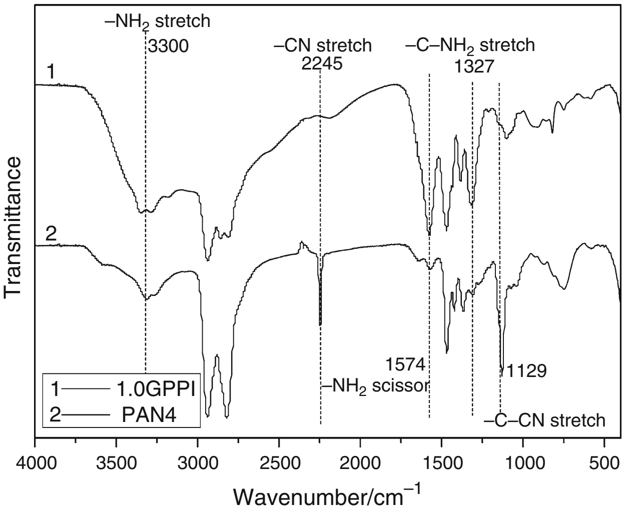


Fig. 1 FTIR spectra of 1.0GPPI and PAN4

around 2245 cm^{-1} due to the vibration of the –C$\equiv$N bonds and another peak emerges around 1129 cm^{-1} arising from the –CH$_2$–CN stretch. These changes in the FTIR spectra indicate that the primary amine groups of 1.0GPPI have preferentially reacted with the double bonds of acrylonitrile, yielding the CNCH$_2$CH$_2$-substituted secondary amine functionalities of PAN4.

The molecular structures of PAN4 and 1.0G PPI are further analyzed with ^{1}H-NMR. Figure 2 shows the ^{1}H-NMR spectra of 1.0GPPI and PAN4, wherein two resonances associated with –NH$_2$ groups can be detected: the signal around 1.25 ppm for the protons of primary amine groups (–N$\underline{H}_2$) and another at 2.68 ppm for the protons of the adjacent units (–C$\underline{H}_2$NH$_2$). On the other hand, the resonance of the –N$\underline{H}$CH$_2$CH$_2$CN protons of PAN4 occurs at a lower field (higher chemical shift value) with dramatically decreased single intensity compared with the –NH$_2$ groups of 1.0G PPI, while the signal for –N$\underline{H}_2$ at 2.68 ppm almost completely vanishes, and the strong resonances for –C$\underline{H}_2$NHCH$_2$CN units appear at 2.89 ppm. These remarks indicate that the majority of the –NH$_2$ functionalities of 1.0G PPI have preferentially reacted with acrylonitrile, producing the CNCH$_2$CH$_2$-substituted secondary amine functionalities of PAN4, which accords with our previous conclusion drawn from the FTIR spectra (Fig. 1).

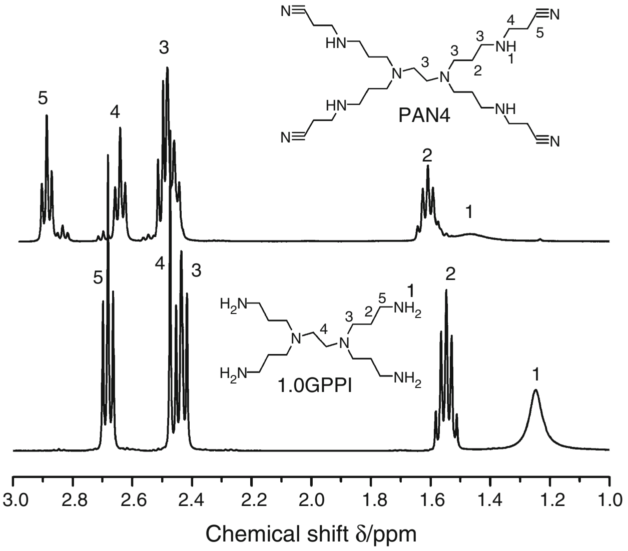


Fig. 2 ^{1}H-NMR spectra of 1.0GPPI and PAN4

Nonisothermal curing kinetics

Theoretical aspects

DSC is a prevalent analytic technique for studying curing reaction of thermosetting polymers due primarily to its great accuracy and easy sample preparation. Curing processes of epoxy resins involve ring-opening of epoxy functionalities with release of a large amount of reaction heat which can be measured precisely with a DSC. In DSC kinetics of epoxy resins, the reaction heat is directly proportional to reacted epoxy groups, so that fractional conversion α reaction rate dα/dt can be expressed by [21–23]

$$\alpha = \frac{\int_0^t \mathrm{d}H\mathrm{d}t}{\int_0^{t_\mathrm{f}} \mathrm{d}H\mathrm{d}t} \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

where H is the heat flow, t_f is the time to completion of cure, t is the reaction time, $f(\alpha)$ is the model-dependent function of α or reaction model, and $k(T)$ is the reaction rate constant which follows the Arrhenius relation (Eq. 3).

$$k(T) = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{3}$$

In Eq. 3, A denotes the preexponential factor or the frequency factor, E_a is the apparent activation energy, and R is the universal gas constant.

On the basis of Eq. 2, a number of semiempirical kinetic models have been proposed and frequently used to describe reaction kinetics of epoxy polymerizations [24–26]. In this situation, a crucial question arises about how to determine a proper kinetic model and how to calculate model-related parameters. To meet this, Málek [26–28] has advanced a criterion of great value for guiding selection of reaction model and computing involved kinetic parameters for a thermally stimulated physical or chemical process under linear temperature programs. A brief introduction to the Málek method is as follows.

According to the Málek method, global activation energy E_a for a nonisothermal process should be estimated previously with another method; for this purpose, the Kissinger method is most frequently used in nonisothermal reaction kinetic studies of epoxy resins. Specifically, when a thermal process proceeds at various linear heating rate β, we have [29]

$$\ln\left(\frac{\beta}{T_p^2}\right) = \text{Const.} - \frac{E_a}{RT_p} \quad (4)$$

where β is the heating rate, and T_p is the peak exothermic temperature at a given heating rate β.

According to Eq. 4, a series of nonisothermal DSC runs at different heating rates must be carried out to link β to T_p. Then, one can construct a linear graph of ln (β/T_p^2) against $1/T_p$, and resulting slope gives rise to E_a. Subsequently, two special functions, $y(\alpha)$ and $z(\alpha)$ (Eqs. 5 and 6), can be established as the diagnostic signatures for proper selection of kinetic models.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp(x) \quad (5)$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \quad (6)$$

In Eqs. 5 and 6, x is the reduced activation energy (E_a/RT) and term $\pi(x)$ is the temperature integral which can be well approximated with Eq. 7 [30–32]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (7)$$

From contours and peak conversions (α_M, α_p^∞) of $y(\alpha)$ and $z(\alpha)$ functions in combination with α_p for the maximum reaction rate, one can determine an appropriate reaction model, and subsequently calculate model-related parameters according to a set of specific computing methods recommended by Málek. Nowdays, many different workers have successfully used the Málek method to study reaction kinetics of different epoxy reaction systems [9, 10, 28, 33–46], justifying its wide applicability in epoxy nonisothermal reaction systems. In this work, we also apply this method to the nonisothermal reactions of DGEBA/1.0GPPI and DGEBA/PAN4.

Curing reaction of epoxy–amine systems

The nonisothermal reactions of the epoxy–amine systems are investigated with the dynamic DSC technique at a series of heating rates of 5, 10, 15, and 20 °C/min, and the recorded DSC curves are demonstrated in Fig. 3. Clearly, only a single exothermic peak appears for each nonisothermal run, which indicates that the primary or secondary amine functionalities of the curing agents (1.0GPPI and PAN4) react with DGEBA simultaneously, and the difference in their reactivity for the same curing agent is not significant [17]. Hence, we can conclude that both of the nonisothermal reactions could be considered as a single kinetic process.

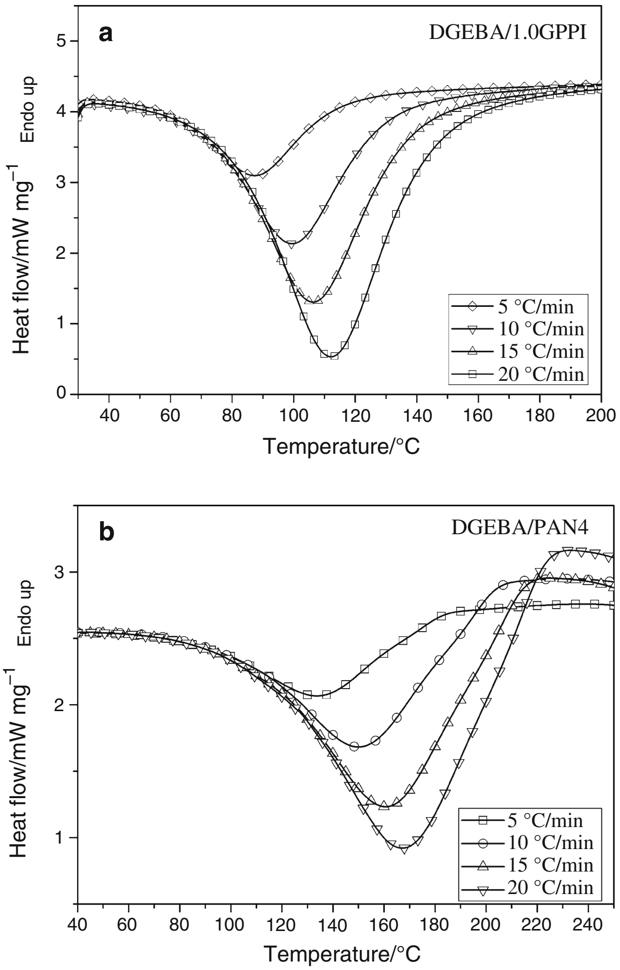


Fig. 3 DSC curves of DGEBA/1.0GPPI and DGEBA/PAN4 at different heating rates

In general, as the heating rates increase, the DSC curves shift to a higher temperature range with systematically increased T_p; however, the reaction heat remains relatively constant (Table 1). The reaction heat of the two epoxy–amine reaction systems is close to the typical value (98–122 kJ/mol) gathered from a considerable number of pure epoxy–amine reaction systems [7, 9, 10, 21, 47, 48]. Here, T_p of DGEBA/PAN4 is considerably higher than that of DGEBA/PAN4 for the same heating rate, but the reaction heat of the former is slightly lower than that of the latter. These results probably stem from the substituent effect of –CN functionalities whereby the electron density on the nitrogen atoms decreases, thus moderately suppressing the enthalpy change associated with the epoxy ring opening. Thus, we conclude that PAN4 can cure the

Table 1 Characteristic parameters obtained from nonisothermal DSC traces of DGEBA/1.0GPPI and DGEBA/PAN4

Formulation	β/°C min^{-1}	T_p/°C	ΔH/kJ mol^{-1}
DGEBA/1.0GPPI	5	87.9	−118.6
	10	99.9	−121.3
	15	106.6	−120.8
	20	112.5	−119.5
DGEBA/PAN4	5	133.6	−95.4
	10	150	−94.0
	15	160.7	−103.4
	20	167.1	−97.7

epoxy resin slowly with alleviated heat release rate compared with the 1.0GPPI control, therefore facilitating the processing and handling of epoxy resins.

Reaction activation energy

According to the Kissinger method, T_p and β (Table 1) were transformed into relation between $\ln(\beta/T_p^2)$ and $1/T_p$, yielding a straight line with excellent linear correlation (Fig. 4). As a result, E_a is 59.7 for DGEBA/1.0GPPI and 53.9 kJ/mol for DGEBA/PAN4 determined from the resulting slopes, which is also in the typical range of epoxy–amine polymerizations [21], likely indicating that the essential ring-open mechanism of the epoxy–amine reactions is little changed. Noticeably, the DGEBA/PAN4 system has a slightly higher E_a value than that for DGEBA/1.0GPPI, which is instinctively inconsistent with the reactivity of the curing agents as suggested by the order of the T_p values for the same heating rate. A possible explanation for this unexpected result is that DGEBA/PAN4 ($\alpha_{gel} = 0.577$) has a higher gel conversion than DGEBA/1.0GPPI ($\alpha_{gel} = 0.378$) [49], which may result in the diffusion of reactive functionalities much easier, thus decreasing the energetic barrier for the diffusion and further lowering the overall apparent activation energy. More importantly, this finding implies that the global activation energy for an epoxy–amine reaction is not always changing in the same way with the macroscopic reaction rates and reactivity of curing agents towards epoxy resins. Therefore, when using apparent activation energies to infer reactivities of epoxy curing agents, we must treat it with great caution (Table 2).

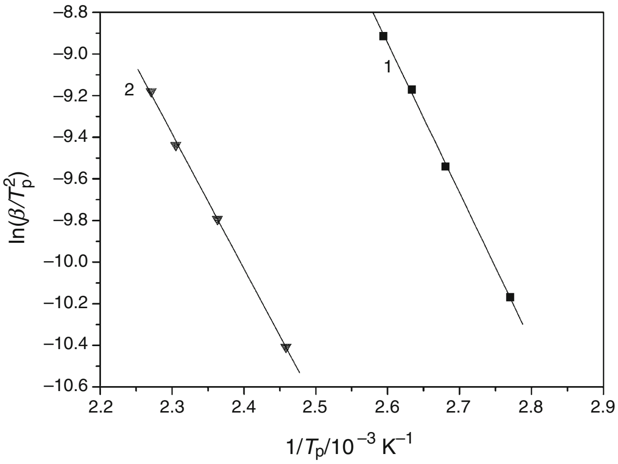


Fig. 4 Kissinger plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for calculating activation energies. *1* DGEBA/1.0GPPI; *2* DGEBA/PAN4

Table 2 Reaction activation energies and corresponding linear regression coefficients of Kissinger plots of DGEBA/1.0GPPI and DGEBA/PAN4

Formulation	E_a/kJ mol^{-1}	Regression coefficient
DGEBA/1.0GPPI	59.7	0.9996
DGEBA/PAN4	53.9	0.99955

Rate equation and modeling

Having known the E_a value, then we can use the Málek method to determine a reaction model. Introduction of the value of $d\alpha/dt$, E_a, T, and β into Eqs. 5 and 6 results in the explicit $y(\alpha)$ and $z(\alpha)$ functions, and then we can readily obtain the values of α_p, α_p^∞, and α_M which are summarized in Table 3. Clearly, they satisfy $0 < \alpha_M < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.632$ simultaneously for each case, suggesting that the two-parameter autocatalytic Šesták-Berggren model (SB(m, n) model) as written by Eq. 8 [50] is probably able to give a better description of the nonisothermal reactions considered here.

Table 3 Characteristic conversions α_p for maximum reaction rate, α_M and α_p^∞ values for $y(\alpha)$ and $z(\alpha)$ functions, and n, m and $\ln A$ values for SB(m, n) model

Formulation	β/°C/min	α_p	α_M	α_p^∞	n	m	$\ln A$/min^{-1}
DGEBA/1.0GPPI	5	0.508	0.207	0.529	1.455	0.378	19.162
	10	0.509	0.194	0.535	1.484	0.358	19.092
	15	0.503	0.184	0.527	1.529	0.344	19.096
	20	0.507	0.188	0.524	1.564	0.362	19.090
DGEBA/PAN4	5	0.587	0.0704	0.623	0.857	0.0603	14.349
	10	0.589	0.0589	0.618	0.828	0.0488	14.313
	15	0.590	0.0570	0.619	0.876	0.0499	14.297
	20	0.589	0.0547	0.619	0.866	0.0474	14.342

Table 4 Rate equations for nonisothermal reactions of DGEBA/1.0GPPI and DGEBA/PAN4

Formulation	Reaction rate equation
DGEBA/ 1.0GPPI	$\frac{d\alpha}{dt} = 1.99 \times 10^{8} \exp\left(\frac{-59730}{RT}\right) \alpha^{0.368} (1-\alpha)^{1.508}, \quad \alpha \in [0, 1]$
DGEBA/ PAN4	$\frac{d\alpha}{dt} = 1.66 \times 10^{6} \exp\left(\frac{-53930}{RT}\right) \alpha^{0.0516} (1-\alpha)^{0.857}, \quad \alpha \in [0, 1]$

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^{m} (1-\alpha)^{n} \tag{8}$$

In Eq. 8, *m* and *n* are the reaction orders, *A* is the pre-exponent factor, and *x* is the reduced activation (E_a/RT). After a logarithmic transformation, Eq. 8 can be rearranged in the following fashion:

$$\ln[(d\alpha/dt)\exp(x)] = \ln A + n \ln\left[\alpha^{m/n}(1-\alpha)\right] \tag{9}$$

where *m*/*n* equals $\alpha_M/(1-\alpha_M)$ (Table 3) according to references [27, 28]. Thus, according to Eq. 9, *n* and ln *A* can be determined from the slope and intercept of a linear plot of $\ln[(d\alpha/dt)\exp(x)]$ versus $\ln[\alpha^{m/n}(1-\alpha)]$ for $\alpha \in [0.1, 0.9]$, and the estimated values of *m*, *n*, and ln *A* are summarized in Table 3. Direct substitution into Eq. 8 of the averaged values of these parameters and obtained E_a yields the ultimate rate equations; see Table 4. Then, the model-predicated reaction rates and the experimental data are compared in Fig. 5 from which we can find that they are in good agreement. Therefore, we can generalize that the SB(*m*, *n*) model is able to well describe the nonisothermal reaction rates of DGEBA/1.0GPPI and DGEBA/PAN4.

Looking closer to Table 3, we can find that *m* and *n*, especially *m*, for DGEBA/PAN4 are much smaller than those for DGEBA/1.0GPPI, which likely indicates the rapid decrease in the reaction rate. Noticeably, the decrease in the *m* values for DGEBA/PAN4 also suggests that PAN4 likely results in the epoxy reaction shifting from the two-step autocatalytic to the single-step non-autocatalytic mechanisms to some extent [33]. Our findings are somewhat similar to the cases of hyperbranched aliphatic epoxy–amine polymerizations where the autocatalytic mechanism seemed to be less important [51]. A possible explanation for this finding is that the $-CH_2CH_2CN$ substituents of PAN4 could solvate the –OH groups present in the reaction system, thus weakening the autocatalytic effect of the –OH functionalities on the further epoxy–amine reaction.

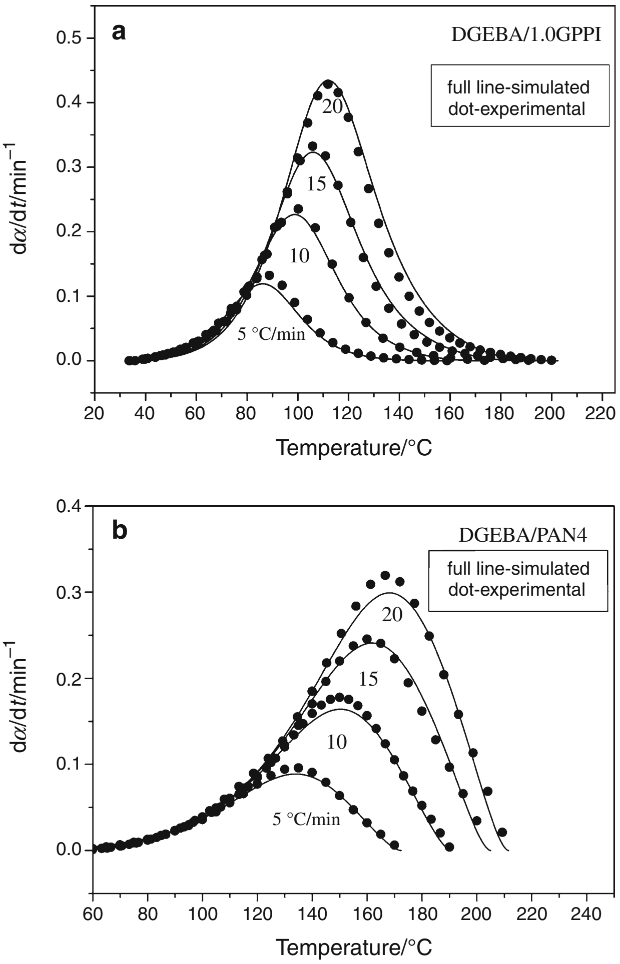


Fig. 5 Comparison of experimental rates and the predicated from SB(*m*, n) model. **a** DGEBA/1.0GPPI and **b** DGEBA/PAN4

To quantitatively inspect the influence of the molecular structure of 1.0GPPI and PAN4 on the reactivity of the resulting epoxy systems, the reaction rate constant for the different temperature *k*(*T*) are calculated with Eq. 3 and compared in Table 5. Evidently, *k*(*T*) of the DGEBA/PAN4 system is generally more than 10 times lower than that of the DGEBA/1.0GPPI system at the same temperatures, which corresponds to the dramatic decreased reactivity of PAN4. This observation probably results from the $-CH_2CH_2CN$ substituents on the amine functionalities which can markedly lower the electronic density of nitrogen atoms of the substituted amine functionalities due to their strong electron withdraw effect with respect to the amine functionalities, further lowering the nucleophilicity of PAN4 to the epoxy rings. In other words, the electronic-withdraw $-CH_2CH_2CN$ substituents on the amine groups largely play a decisive role in the reactivity of PAN4 towards epoxy resins.

In conclusion, we can rationally generalize that reactivity of the curing agents derived from dendritic polyamines can be effectively tailored by the chemical attachment of the $-CH_2CH_2CN$ substituents onto their primary amine functionalities, still leaving adequate reactive amine hydrogen functionalities (N–H) to trigger crosslink of epoxy resins.

Table 5 Rate constants $k(T)$ of DGEBA/1.0G PPI and DGEBA/PAN4 for different temperatures

Formulation	Rate constant k/min^{-1}						
	40 °C	60 °C	80 °C	100 °C	120 °C	140 °C	160 °C
DGEBA/1.0PPI	0.0217	0.0859	0.291	0.867	2.31	5.59	12.5
DGEBA/PAN4	0.00168	0.00581	0.0175	0.0468	0.1134	0.252	0.520

Conclusions

A novel acrylonitrile-capped aliphatic polyamine with dendritic structure (PAN4) has been readily synthesized under the mild reaction conditions. The FTIR and ^{1}H-NMR analyses confirmed that PAN4 had the designed molecular structure and composition. Moreover, the global activation energies for the DGEBA/1.0GPPI and DGEBA/PAN4 reactions were 59.7 and 53.9 kJ/mol, respectively, and the reaction rates could be well described with the two-parameter autocatalytic model (SB(m, n)). The quantitative analysis of the reaction rate constant revealed that PAN4 could cure DGEBA at a greatly decreased rate compared with 1.0GPPI by a factor a more than 10, due to the electron withdraw effect of the –CH_2CH_2CN functionalities. Furthermore, PAN4 was likely to suppress the autocatalytic effect of newly formed –OH groups on the epoxy-amine reaction, as indicated by the dramatic reduce in the reaction order m in the rate equation for DGEBA/PAN4. In conclusion, PAN4 may find practical usage as a novel curing agent for epoxy resins with long pot life and excellent processability, and our further work will focus on the properties of cured DGEBA/1.0GPPI and DGEBA/PAN4 networks.

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