Polymer Chemistry

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer Chemistry

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Journal Name

ARTICLE

Study on the chain propagation of benzoxazine

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The chain propagations of Bisphenol A-aniline benzoxazine (defined as BA-a) polymerized by thermal induction and in the presence of various catalysts or curing agents during the curing process before gelation were investigated in this paper. DSC, Gel time test and GPC were used to measure the curing behavior, number-average molecular weight($\overline{Mn}$), glass transition temperature(Tg), gel time(t_{gel}) and curing conversion(α) of different benzoxazine systems. By comparing the experimental results($\overline{Mn}$ and Tg) with the models of step polymerizations and chain polymerizations proposed by Flory et al., three kind of chain propagation of benzoxazine were observed and confirmed. The step polymerization occurred in the thermal induction or in the presence of catalyst N, N-dibenzylaniline (tAm), and then the non-living chain polymerization and the living chain polymerization appeared, respectively, when Indole (Id) and other additives such as phenol (tBp), acid (HA) and imidazole (IMZ) etc. were added in the benzoxazine as catslysts or curing agents. Moreover, the relationship between chain propagation and curing kinetics of benzoxazine were also eatablised. For the chain propagation of benzoxazine systems are the step polymerization, the non-living chain polymerization and the living chain polymerization, the conversion of the gel point (α_{gel}) is almost equal to, less than and greater than the value of the conversion at which polymerization rate reaches to a maximum(α_{max}), respectively. The results may contributed to a better understanding of the polymerization mechanism of benzoxazine and provide new approaches to an effective control of the polymerization kinetic and growth crosslink structures of benzoxazine.

Introduction

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. Thus, the chain propagation is one of core problems in the preparation of the polymers. To further understand the chain propagation mechanisms, Flory et al. [1, 2] divide various polymerizations into step polymerizations and chain polymerizations based on the polymerization mechanisms and polymerization kinetics. The feature curve models of number-average molecular weight ($\overline{Mn}$) vs conversion related to the chain propagation was also established. Step and chain polymerizations differ in several features, but the most important difference is in the species that can react with each other. Another difference is the manner in which polymer $\overline{Mn}$ depends on the extent of conversion. Step polymerization proceeds by the stepwise reaction between functional groups of reactants and the size of the polymer molecule increases at a relatively low pace in such polymerization. One proceeds from monomer to dimer, trimer, tetramer and so on until eventually large-sized polymer molecules have been formed. The characteristic plot of $\overline{Mn}$ vs conversions for the step polymerization is shown in Figure 1 curve 1. The situation is quite different in chain polymerization where the polymer growth takes place by monomer reacting only with the reactive center. In addition, according to the relationship between the molecular weight and the extent of conversion, the chain polymerization can be further divided into the living chain polymerization and the non-living chain polymerization, and the

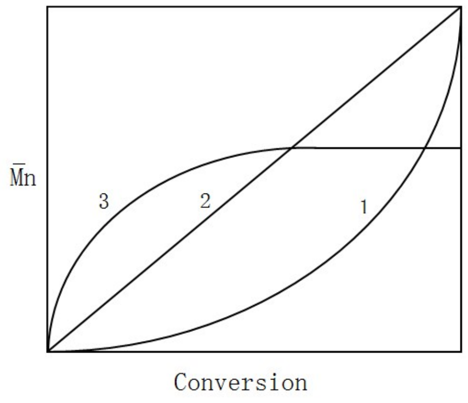


Figure 1 Molecular weight vs conversion diagrams of the step polymerization (1), the living polymerization (2) and the non living polymerization (3)

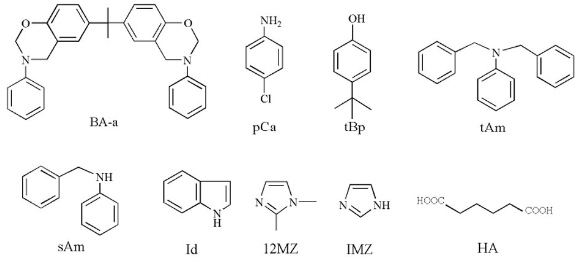
relationship between the molecular weight and the conversion is shown in Figure 1 curve 2 and curve 3, respectively.[3-7]. Kojima et al.[4] reported that the number-average molecular weight of the isobutyl vinyl ether in the presence of the zinc halide increased in direct proportion to monomer conversion and independent of polymerization temperature, and they used the so called “monomer addition” experiments to demonstrate this polymerization was the living chain polymerizaition. Moreover, Sigwalt et al.[6, 7] have studied the chain propagation mechanisms of cumyl methyl ether/ titanium tetrachloride. The results obtained are consistent with previous reports. However, the living chain polymerization can transform into the non-living chain polymerization when the termination and transfer reactions occur in the system[8]. At present, researches on the chain propagation mainly focus on the thermoplastics, but studies on that of thermosetting resins are so rare mainly because the chemical reactions are very complex during the curing for the thermosetting resins. In addition, the formation of inmeltable and insoluble network after the gel reaction makes the molecular weight difficult to test, which is also a problem to study the chain propagation of the thermosetting resins. Thus, the chain propagation of thermosetting resins can only be studied before the gelation.

Benzoxazine is a new class of high performance thermosetting resins. It attracts much attention due to their attractive properties such as considerable molecular design flexibility[9-13], excellent heat resistance and mechanical properties[14-16], lower water absorption[17], non release of byproducts and near zero linkage shrink or volumetric expansion during the cure[18, 19]. They have shown high potential to be applied to many important areas such as automotive industries and aerospace. However, the crosslink density of polybenzoxazines is relatively low[20, 21]. Thus, in order to achieve a good molecular understanding of the polymer structure-properties relationships. It is of great importance to understand the mechanistic pathways. Ishida group and Gu group have done a lot of extensive works in benzoxazine chemistry in recent years[22-34]. On the base studies of various cationic, anionic and radical initiators, they have suggested that ring opening polymerization of the benzoxaine proceed through a cationic mechanism. Moreover, they have also found that the ring opening polymerization of benzoxazine in different conditions gave the corresponding polymers having the different crosslink structures[23, 26, 27, 30]. However, previous studies on the polymerization mechanism of benzoxazine are mainly from the perspective of the structural characterization or the molecular stimulation. So far from the angle of kinetics there is no report about the chain propagation of benzoxazines during the curing reaction and its macroscopic rules.

The crosslink structures and final properties of thermosetting resins depend significantly on the chain propagation, curing behavior etc. Thus, the study of the chain propagation can contribute to a better knowledge of process development and an improvement of the quality of final products relate to the structures of the polymers network. In this paper, the chain propagations of benzoxazine polymerized by thermal induction and in the presence of various catalysts or curing agents before gelation were studied firstly. Differential Scanning Calorimetry (DSC), Gel time measurment and Gel Permeation Chromatography (GPC) were used to measure the curing behavior, number-average molecular weight, glass transition temperature, gel time and curing conversion of different benzoxazine systems. By comparing the experimental results with the models of step polymerization and chain polymerization proposed by Flory et al., the chain propagation of each system was confirmed and the macroscopic rules were summarized. At same time，the relationship between chain propagation and curing kinetics of benzoxazine were also discussed.

Experimental

All regents were used as received. Indole (Id), 1, 2-dimethylimidazole (12MZ), P-tert-butyl phenol (tBp), N, N-dibenzylaniline (tAm), N-phenylbezylamine (sAm), Sodium iodide (NaI), parachoroaniline (pCa), hexane diacid (HA) and imidazole (IMZ), with purities great than 99%, were purchased from Aladdin reagent or Chengdu Kelong chemical reagent (China). The structures of the regents are shown in scheme 1.



Scheme 1 The structures of the regents

Synthesis and purify of benzoxazine

Bisphenol A-aniline benxozaine (defined as BA-a) was synthesized and purified according to the procedures described earlier[31]. BA-a: white needle-like crystals (yield 93%); Melting point(DSC): 115℃; FTIR: 946cm^{-1} (oxazine ring), 1030cm^{-1} and 1234cm^{-1} (C-O-C stretching mode of oxazine ring), 1498cm^{-1} (1, 2, 4-trisubstitution of the benzene), 2870cm^{-1} and 2960cm^{-1} (-CH_3-streching vibration); ^{1}H NMR（DMSO-d_6）: 6.61-7.22ppm (Ar-H), 5.40 ppm (O-CH_2-N), 4.61 ppm (Ar-CH_2-N), 1.53 ppm (-CH_3).

Samples preparation

BA-a was melted in a glass container at 115^{o}C, then 10% mol of catalyst x was added (5% mol for HA) and stirred for 3 min. After that, the sample was refrigerated to avoid any further curing reaction, and the sample defines as BA-a-x.

The gel samples were prepared by using a gel time testing instrument. The sample cell of the instrument was first heated to a required temperature. Then, about 1 g resin was put on the cell and spread to a disk with a stir-stick. The sample was kneaded by pressing it uniformly about every second until the sample was no longer stuck to the spatula. After that, the gel was taken out quickly and stored in a refrigerator for further characterizations.

Samples for DSC and GPC analysis: BA-a and BA-a-x were polymerized on a gel test instrument at 200^{o}C. Small portions of the sample were obtained from the sample cell at different time intervals and then used to DSC and GPC analysis.

Characterizations

Differential Scanning Calorimetry (DSC) was performed on a TA Instruments DSC Q20 using nitrogen purge and an empty aluminum pan as a reference. For the non-isothermal test, the heating rate was 10 ^{o}C/min; For the isothermal experiments, the samples were palced in the cell at 40 ^{o}C and then the temperature was raised to the set temperature with a scanning rate of 100 ^{o}C/min and the data acquisition was then initiated. After the DSC curve reached the baseline level again, the sample was cooled rapidly to 40 ^{o}C. The samples with 3-4mg were used in the DSC test. The temperature at half extrapolated tangents of the step transition midpoint was used as glass transition temperature (Tg). The conversion α, was calculated by equation $\alpha=1-H_r/H_t$, where H_r was the residual heat of polymerization of a sample, H_t was the total heat of polymerization of a sample; The conversion at the gel point (α_{gel}) was calculated by equation $\alpha_{gel}=1-H_{gel}/H_t$, where H_{gel} is the residual heat enthalpy of the gel samples, H_t is the total heat of polymerization; The polymerization rate (dα/dt) of a system was calculated by equation: $d\alpha/dt=dQ/dt\bullet H_t^{-1}$, where dQ/dt is heat flow detected by isothermal DSC, t is the curing time, H_t is the total heat of reaction.

Fourier Transform Infrared Spectroscopy (FTIR) was obtained on a Nicolet Magna 650 instrument. The range was 4000-400cm^{-1} with a resolution of 4cm^{-1}. The samples were prepared by KBr pellets.

^{1}H NMR measurements were carried out using a Bruker TD-65536 NMR (400 MHz), with Deuterium dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the internal reference.

Number-average molecular weight was estimated by Gel Permeation Chromatograph (GPC) on a Tosoh HLC-8320 system, equipped with two consecutive polystyrene gel columns (TSK gel super HZM-M 6.0*150mm and TSK gel Super HZ3000 6.0*150mm) and refractive index (RI) and ultraviolet (UV, 254 nm) detectors, using THF as a eluent, flow rate 0.6 mL/min, calibrated with polystyrene standards.

Results and discussion

Curing behavior of BA-a

It is believed that the chain propagation of the polymers is closely linked to its curing behavior. The changes in the curing behavior of the resin system lead to the corresponding changes in its chain propagation[35, 36]. The curing behavior of the BA-a and BA-a-x was investigated by DSC and Gel time test. The DSC thermograms are shown in Figure 2. BA-a shows a typical polymerization exothermic peak centered at 259^{o}C, but the exothermic peak temperature shifted to 254 ^{o}C, 226 ^{o}C, 251 ^{o}C, 223 ^{o}C, 229 ^{o}C, 245 ^{o}C, 231 ^{o}C and 216 ^{o}C in the presence of tAm, Id, sAm, IMZ, 12MI, pCa, HA, tBp and NaI as the catalysts or curing agents, respectively. It means that the curing behavior of BA-a changed by adding various additives. To clarify this further, we next investigated the gel time (t_{gel}) of BA-a and BA-a-x at different temperatures through the Gel time test and the results are summarized in Table 1. The t_{gel} of BA-a at 200^{o}C, 210^{o}C and 220^{o}C is 3109s，1685s and 1030s, respectively. The gel times of BA-a were shorted in various degree with the addition of tAm, Id, IMZ, 12MI, HA, sAm, tBp, pCa or NaI. The obtained results are in good agreement with the DSC results, which may mean that the change of the chain propagation of benzoxazine has taken place due to the changes of the curing behavior. In order to further illustrate the results mentioned above, α_{gel}, the conversion at the gel point, which is one fundamental parameter for the processing of thermosetting resins, was investigated by gel time tests and DSC analysis.

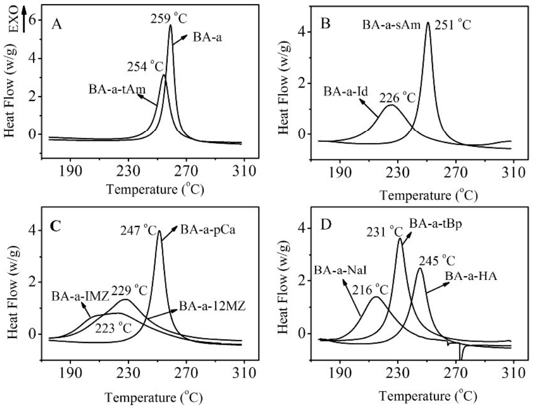


Figure 2 the DSC curves of BA-a and BA-a-x

Table 1 The α_{gel} and t_{gel} results of BA-a and BA-a-x systems

Systems	200℃		210℃		220℃	
	α_{gel} (%)	t_{gel}^{200} (s)	α_{gel} (%)	t_{gel}^{210} (s)	α_{gel} (%)	t_{gel}^{220} (s)
BA-a	37.9	3109	41.6	1685	42.8	1030
BA-a-Id	20.4	883	22.6	514	18.7	299
BA-a-pCa	31.1	2674	30.7	1463	29.5	820
BA-a-IMZ	32.4	410	33.2	197	34.9	133
BA-a-12MZ	32.2	977	32.5	625	32.8	304
BA- a-tBp	40.4	937	38.1	409	38.8	361
BA- a-tAm	39.9	3081	40.4	1423	43.7	951
BA- a-HA	40.1	2084	42.1	1394	40.9	676
BA- a-sAm	44.3	2330	46.5	1380	40.9	790
BA- a-NaI	37.0	1776	37.8	1182	39.1	704

α_{gel}, the conversion at the gel point; t_{gel}, the gel time.

The t_{gel}s and α_{gel}s for BA-a and BA-a-x at different temperature are summarized in Table 1. The α_{gel} is 37.9% for the thermally induced ring opening polymerization of BA-a at 200^{o}C, and it can be significantly changed in a large range by adding various catalysts or curing agents. As an example, the presence of Id is accompanied by a large decrease of the gel conversion, to 20.4%, which is far below those observed in the case of neat resin. In addition, all systems exhibit the similar behavior at different test temperatures (Table 1). These results illustrate that the chain propagation of benzoxazine was changed in the presence of various catalysts or curing agents. In order to make the results mentioned above more clear, the plots of t_{gel} vs α_{gel} of the systems at 200°C are exhibited in Figure 3. There are obvious changes in t_{gel} and α_{gel} of BA-a in the presence of various additives. Moreover, the relationship between t_{gel}s and α_{gel}s can be classified into three basic types, which may be associated with the chain propagation of benzoxazine during the curing reaction. This will be discussed in detail later in this paper.

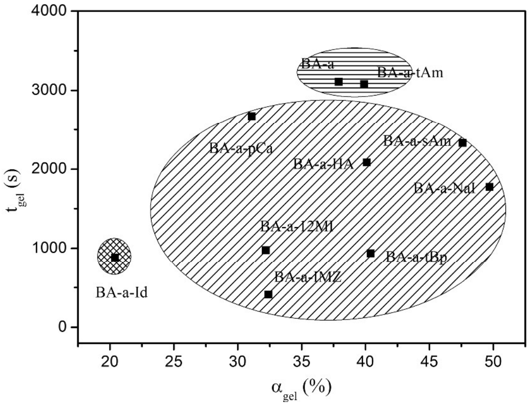


Figure 3 t_{gel} vs α_{gel} of BA-a and BA-a-x at 200 °C

The chain propagation models of BA-a during the curing process

The number-average molecular weight ($\overline{M_n}$) and the conversion of each system at different curing stages before gelation were investigated by GPC and non-isothermal DSC measurements based on the chain propagation models proposed by Flory et al. The plots of $\overline{M_n}$ as a function of conversion for BA-a, BA-a-Id, BA-a-IMZ and BA-a-NaI are shown in support information Fig.SI 1. The different variation rules of $\overline{M_n}$ vs conversion for the four systems mean that their chain propagations are different. The results are in good agreement with that in section 3.1. Since the experimental process of GPC measuring on $\overline{M_n}$ of the samples is not only complicated and time-consuming, but also limited by many factors, a simple and effective method was used in this paper[37-39], that is, the relationship between $\overline{M_n}$ and conversion was investigated by measuring the Tg at different conversions (The Tgs of BA-a at different curing degree can be easily observed by DSC and the result is shown in Fig.SI 2). A good linear relationship between Tg and $\overline{M_n}$ before gelation have been detected for the BA-a, BA-a-Id, BA-a-IMZ and BA-a-NaI systems, which is shown in support information Fig.SI 3. This result further illustrates that the relationship between Tg and conversion can be qualitatively used to describe the relationship between $\overline{M_n}$ and conversion of the benzoxazine systems.

The plots of Tg as a function of conversion for BA-a and BA-a-x before the conversion reaches to the α_{gel} are shown in Figure 4 and Figure 5, respectively. As is shown in Figure 4, The Tg increases slowly when the conversions of BA-a and BA-a-tAm are lower (the conversion less than 15%) and increases quickly when the conversions are higher (the conversion more than 15%). Compared to that of BA-a and BA-a-tAm, the relationship between the Tg and the conversion of BA-a in the presence of Id, IMZ, 12MI, HA, sAm, tBp, pCa or NaI has been changed. As is shown in Figure 5A, the Tg of BA-a-Id increases rapidly at first (the conversion lower than 8%), then it remains approximately constant until the conversion reached to the α_{gel} (20.4%). In addition, another rule of curve is also detected in Figure 5. The Tg increases linearly with the conversion of BA-a by adding tBp, sAm, NaI, pCa, HA, 12MZ or IMZ. According to the results mentioned above, the plots of $\overline{M_n}$ or Tg as a function of conversion for benzoxazine in Fig.SI 1, Figure 4 and Figure 5 can be classified as three basic types. By comparing above results with the chain propagation models proposed by Flory et al., the following results are obtained: both chain propagations by thermally induced polymerization of BA-a and by catalysis polymerization of BA-a-tAm are the step polymerizations, their plots of molecular weight vs conversion conform to the model shown in Figure 1 curve 1; and the chain propagation of BA-a is the non-living chain polymerization or the living chain polymerization in the presence of Id or other additives (such as tBp, sAm, NaI, pCa, HA, IMZ and 12MZ) as catalysts or curing agents, their plots of molecular weight as a function of conversion conform to the models shown in Figure 1 curve 2 and curve 3, respectively.

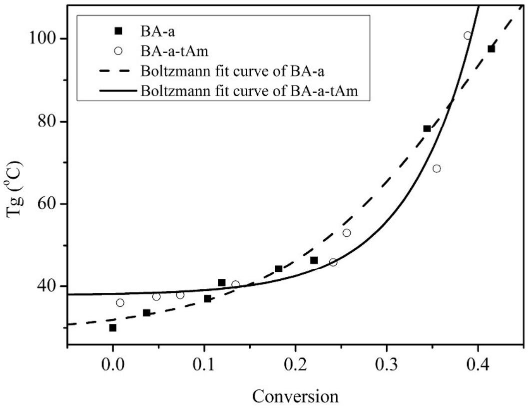


Figure 4 Tg vs conversion curves of BA-a and BA-a-tAm

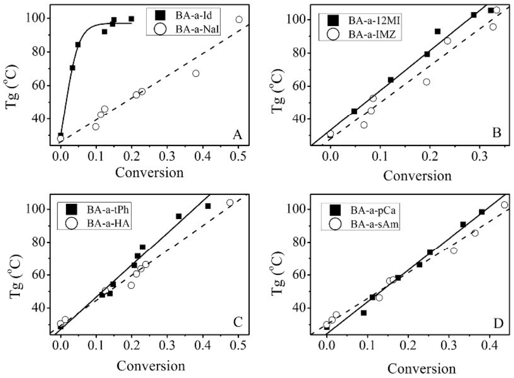


Figure 5 Tg vs conversion curves of BA-a-x systems

Curing kinetics of BA-a

The curing kinetics of thermosetting resins is closely related to their chain propagation mechanisms. A change in the chain propagation of benzoxazine during the curing process resulted in a corresponding change in its curing kinetics. In order to obtain a better knowledge of the chain propagation of benzoxazine, the plots of polymerization rate of BA-a and BA-a-x as a function of conversion (support information Fig.SI 4-Fig.SI 13) and the values of the conversion at the peak of polymerization rate curve (α_{Rmax}, Table 2) for all systems were obtained from the isothermal DSC measurements at 200°C, 210°C and 220°C, respectively. And the chain propagation of benzoxazine during the curing reaction was discussed by comparing the values of α_{gel} with that of α_{Rmax}.

Table 2 The α_{Rmax}.of BA-a and BA-a-x at 200�, 210�and 220�

Sample	200°C α_{Rmax}. (%)	210°C α_{Rmax}. (%)	220°C α_{Rmax}. (%)
BA-a	37.6	41.7	43.0
BA-a-tAm	42.1	41.8	44.0
BA-a-Id	28.9	30.7	28.7
BA-a-NaI	28.6	30.8	31.5
BA-a-IMZ	15.2	9.7	4.4
BA-a-12MI	18.8	18.8	9.6
BA-a-tBp	36.1	38.6	36.4
BA-a-HA	38.7	40.8	39.1
BA-a-pCa	34.6	35.3	35.8
BA-a-sAm	38.4	40.3	37.4

α_{Rmax}: the conversion at which polymerization rate reaches a maximum of the system.

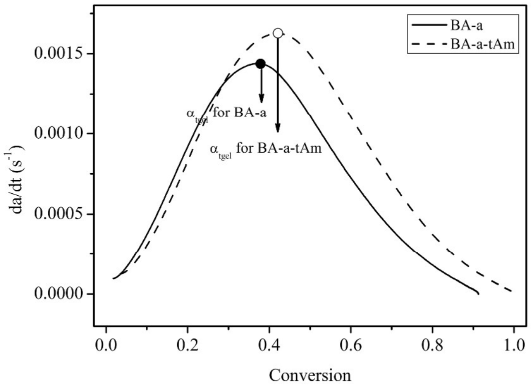


Figure 6 Polymerizatiom rate vs conversion curves of BA-a and BA-a-tAm

In Figure 6 and Figure 7, the plots of polymerization rate vs conversion of BA-a and BA-a-x at 200°C are shown, respectively. For each system, the conversion of the gel point (α_{gel}, the values are shown in table 1) is indicated by vertical arrow on the curve.

It is noteworthy, from the Figure 6, Table 1 and Table 2, that the values of α_{gel} for BA-a and BA-a-tAm at 200°C are 37.9% and 41.6%, respectively, which are almost equal to the values of their α_{Rmax}s (37.6% and 42.1). Compared to BA-a and BA-a-tAm, the BA-a-Id shows a rather different situation, which is reflected by appearance of gelation (α_{gel}=20.4%) before the peak (α_{Rmax}=28.9%) on the polymerization rate curve (Figure 7A and Table 2). In addition, the gel behavior of the BA-a in the presence of tBp, sAm, NaI, pCa, HA, 12MZ or IMZ occurs after the maximum reaction rate (Figure 7 and Table 2). Moreover, all the systems at 210°C and 220°C exhibited the similar situation as that at 200 °C, and the results are presented in Table 2 and support information Fig.SI 4-Fig.SI 13. The results mentioned above indicate that the curing kinetics of BA-a are different from those of BA-a containing the catalysts or curing agents. That is, the chain propagation of the benzoxazine systems is the step polymerization when the gel behavior occurs almost at the peak of the polymerization rate curve ($\alpha_{gel} \approx \alpha_{Rmax}$). For the gel behavior of the system occurs before ($\alpha_{gel} < \alpha_{Rmax}$) and after ($\alpha_{gel} > \alpha_{Rmax}$) the maximum of polymerization rate, the chain propagations of benzoxazine systems are the non-living chain polymerizations and the living chain polymerizations, respectively. The mutual relations between them are shown in Figure 8.

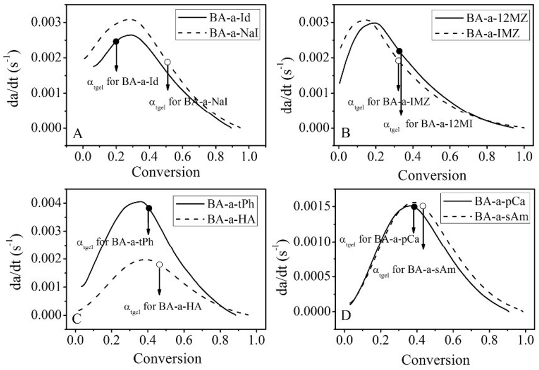


Figure 7 Polymerizatiom rate vs conversion curves of BA-a-x

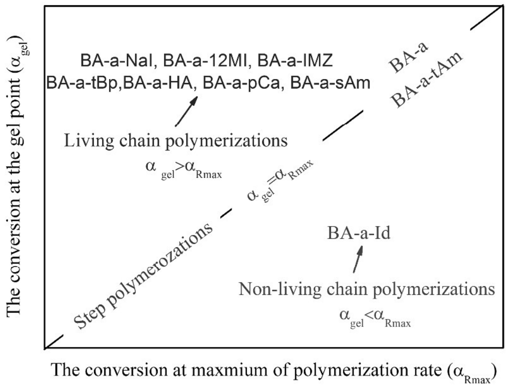


Figure 8 The effect of the α_{Rmax} on α_{gel}

Conclusions

The chain propagations of benzoxazine polymerized by thermal induction or in the presence of various catalysts or curing agents during the curing process before gelation were investigated. By comparing the experimental results with the models of step polymerizations and chain polymerizations proposed by Flory et al., the chain propagations of benzoxazine are confirmed and summarized as three basic types: the chain propagation of the thermally induced polymerization of BA-a and that of catalysis polymerization of BA-a-tAm are the step polymerization, and the chain propagations of BA-a in the presence of Id and other additives (IMZ, 12MZ, HA, sAm, tBp, pCa, NaI, et al.) as the catalysts or curing agents are the non-living chain polymerization and the living chain polymerization, respectively. Moreover, in order to obtain a better knowledge of the polymerization kinetics and growing network structures of benzoxazine, the relationship between chain propagation and the curing kinetics of the system was established. That is, when the chain propagation of benzoxazine systems are the step polymerization, the non-living chain polymerization and the living chain polymerization, respectively, the conversion of the gel point is almost equal to ($\alpha_{gel}\approx\alpha_{Rmax}$), less than ($\alpha_{gel}<\alpha_{Rmax}$) and greater than ($\alpha_{gel}>\alpha_{Rmax}$) the value of the conversion at which polymerization rate reaches to a maximum. The results obtained, not only improve and complement the relevant theory of polymerization mechanism of benxazine, but also lay a good foundation for further study the chain propagation mechanism from more microscopic point of view. Moreover, this research also provided new approaches to an effective control of the crosslink structures and properties of the polybenzoxazines.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Project No.51273119)

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Study on the chain propagation of benzoxazine

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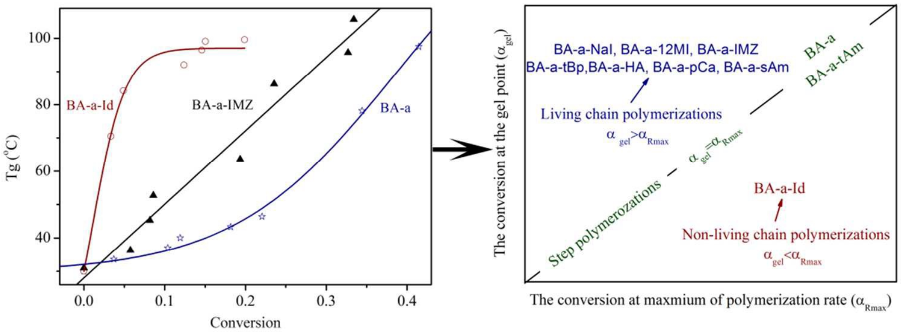
Graphical abstract



Variation of Tg with conversion of step polymerization, living chain polymerization and non-living chain polymerization of benzoxazine during the curing process