Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6763–6772
polymer
www.elsevier.com/locate/polymer

Polymerization of linear aliphatic diamine-based benzoxazine resins under inert and oxidative environments

Douglas J. Allen, Hatsuo Ishida*

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, United States

Received 19 July 2007; received in revised form 24 August 2007; accepted 2 September 2007
Available online 5 September 2007

Abstract

A series of linear aliphatic diamine-based benzoxazine monomers have been studied. Reaction times and purification procedures have been optimized for each individual diamine. The structure of these diamine-based benzoxazine monomers has been characterized by ^{1}H and ^{13}C NMR, and infrared spectroscopy. The rate of polymerization has been studied by Fourier transform infrared spectroscopy as a function of the chain length of the aliphatic amines. The glass transition temperatures (T_g) of the polybenzoxazines from these monomers are also studied. The short chain amine polybenzoxazine exhibits the T_g of around 170 °C. The influence of the polymerization environment for these linear aliphatic diamine-based series of benzoxazine monomers has been studied under air and inert atmosphere. Differential scanning calorimetry is used to determine the melting points of these benzoxazines and the temperature of the peak polymerization exotherm. An anomalous polymerization behavior of ethylene diamine-based polybenzoxazine is also reported.

Keywords: Polybenzoxazine; Linear amine-based benzoxazine; FTIR

1. Introduction

Polybenzoxazines are a class of thermosetting phenolic resins that have been developed over the last decade as an attractive alternative to epoxies and traditional phenolic resins [1–10]. Benzoxazine resins are readily synthesized, either in solution or by a melt-state reaction using a combination of a phenolic derivative, formaldehyde, and a primary amine [11,12]. The unique chemistry of benzoxazines is responsible for a number of inherent processing benefits, including low melt viscosity, no volatile release upon cure, rapid development of properties, and low overall shrinkage. Thermally activated ring-opening polymerization results in a high modulus thermosetting material with excellent thermal, mechanical, and electrical properties [10].

Thermally activated polymerization of monofunctional benzoxazines typically leads to a linear or branched structure with a molecular weight in the order of 500–2000 and is characterized by the presence of a Mannich base bridge [13]. The polyfunctionality required to form an infinite network structure upon polymerization may be achieved through monomer synthesis utilizing either a multifunctional phenolic molecule with a monoamine, or with a multifunctional amine paired with a mono-phenol, examples of which are shown in Fig. 1. However, of these two approaches, the overwhelming majority of polybenzoxazine research published to date has focused almost exclusively on materials in which the phenolic compound, typically a bisphenol, provides this multifunctional core. Despite their additional molecular design opportunities, the subclass of multifunctional amine-based materials has largely been ignored. With a vast number of suitable starting compounds available, multifunctional amine-based polybenzoxazines have tremendous untapped potential in the area of tailoring molecular structure for specific applications. Recently, we reported the synthesis and properties of linear aliphatic diamine-based benzoxazines [14]. Also, an attempt to synthesize aromatic diamine-based benzoxazines has been reported [15].

As is the case with traditional phenolic resins, the brittle nature of polybenzoxazines can sometimes limit their potential applications. This characteristic is a consequence of the rigid

* Corresponding author.
E-mail address: hxi3@cwru.edu (H. Ishida).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.09.003

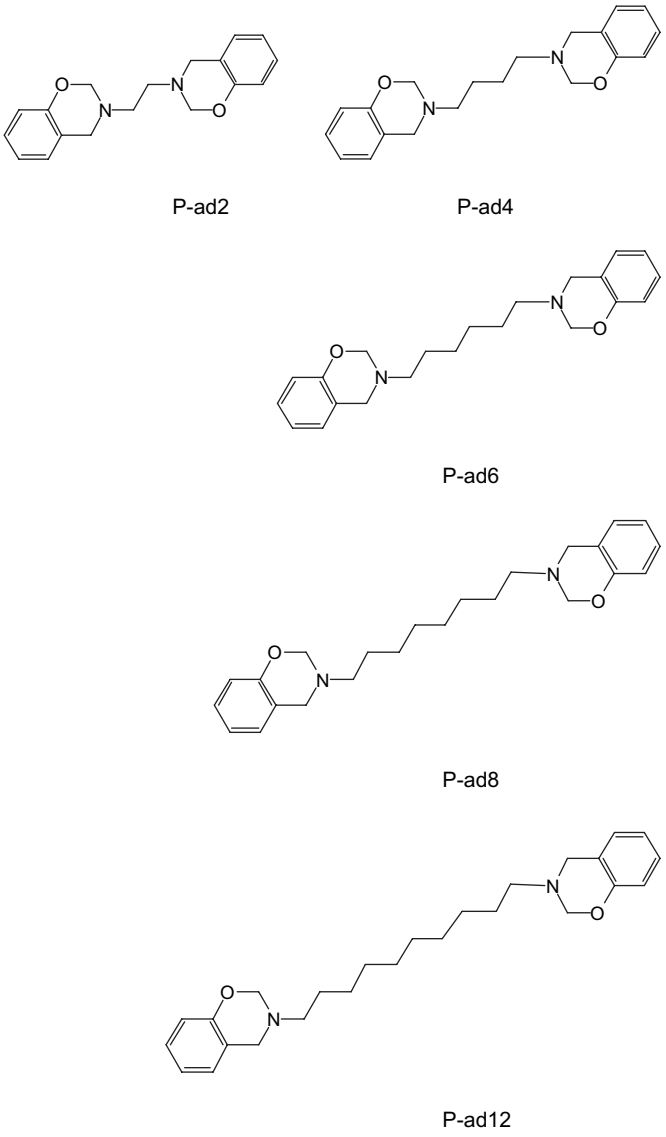


Fig. 1. Structures and nomenclature used for the series of linear aliphatic diamine-based benzoxazine monomers.

bisphenol backbone upon which polybenzoxazines have typically been derived. In order to improve toughness and other mechanical properties, several groups have successfully investigated rubber and thermoplastic polymer modifications of the benzoxazine resins [16–18]. Improvements can also be sought through reactive blending that chemically incorporates a flexible chain such as an epoxy, polycaprolactone, poly(vinylphenol), or polyurethane into the polybenzoxazine matrix structure [3,19–21]. Both of these approaches toward improving the brittleness of the cured material involve the addition of a foreign component into the polybenzoxazine matrix.

This paper seeks to investigate some of the previously unexplored molecular design opportunities that are available by switching difunctionality of the benzoxazine to the amine portion of the structure. In this study, a series of linear aliphatic diamine-based benzoxazines (Fig. 1) will be studied to demonstrate the feasibility of increasing the inherent flexibility of the polybenzoxazine network structure itself.

2. Experimental

2.1. Materials

Phenol (99%) and 1,6-hexadiamine (99.5%) were purchased from the Acros Division of Fisher Scientific, while ethylene diamine (99%), 1,4-diaminobutane (99%), 1,8-diaminooctane (98%), and paraformaldehyde (95%) were obtained from Aldrich Chemical. 1,12-Diaminododecane (99%) was purchased from Fluka. All chemicals were used as received with no further purification. Synthesis of the linear aliphatic diamine-based benzoxazine monomers was performed according to the paper reported elsewhere [14].

2.2. NMR

Both proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopies, Varian Gemini XL-200 spectrometer, operating at a proton frequency of 200 MHz and a corresponding carbon frequency of 50.3 MHz were used to study the structure of the diamine-based benzoxazine monomers. Deuterated chloroform was used as the solvent with all peaks referenced relative to tetramethylsilane (TMS). The ^{1}H spectra obtained using 64 transients and a concentration of 1 wt%, while 1024 transients and a concentration of 5 wt% were used for the ^{13}C spectra yielded sufficient signal-to-noise ratio for the study.

2.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the benzoxazine monomers and polymers were obtained on a Biorad FTS-60A spectrometer with a potassium bromide (KBr) beamsplitter and a deuterated triglycine sulfate (DTGS) detector. The spectrometer was purged with dry nitrogen and operated in transmission mode utilizing the coaddition of 256 scans at a resolution of 2 cm^{-1}. The monomer spectra were obtained from 1–2 mg samples cast from chloroform onto 25 mm KBr plates.

FTIR spectroscopy was also utilized to follow the polymerization of each monomer at 180 °C. The kinetic spectra were obtained using the same spectrometer fitted with a Connecticut Instruments hot cell in which the samples could be heated rapidly and held to within a degree of the set temperature. To minimize thickness changes due to flow, thin films of the benzoxazine monomers were sandwiched between two 20 mm KBr plates. The samples were heated and allowed to stabilize at 120 °C, which will later be shown to be above the melting point of all monomers but low enough to prevent any significant reaction. After thickness appeared to be constant, the cell was rapidly heated at a rate of approximately 30 °C/min. Data acquisition was initiated immediately upon reaching the 180 °C cure temperature. Win-IR Pro kinetic software permitted continuous scanning at a resolution of 2 cm^{-1} with spectral sets of 33 coadded scans stored every minute for the duration of each 150 min cure cycle. A 256 scan, room temperature FTIR spectrum of

each polymer was also taken after the cell had fully cooled at the end of each kinetic experiment.

2.4. Differential scanning calorimetry

The melting points and reaction exotherms of the benzoxazine monomers were measured via differential scanning calorimetry (DSC) utilizing a TA Instruments DSC 2910 calorimeter equipped with a Pressure DSC cell. Thermal data analysis was performed using TA Instruments Universal Analysis software. Benzoxazine samples of approximately 4 mg were scanned in hermetic aluminum sample pans with pierced upper lids. Thermograms were obtained at a heating rate of 10 °C/min over a temperature range of 25–300 °C with the DSC cell pressurized by nitrogen to 2.8 MPa. Curve resolving was performed in Grams/32 software (Galactic Industries) using a mixed Gaussian–Lorentzian function until convergence of least-squares curve fitting.

3. Results and discussion

3.1. Synthesis

A solventless, melt-state reaction [22] is typically the synthetic procedure of choice for the preparation of benzoxazine monomers, primarily due to its simplicity and its purity of products. However, the high reactivity of the linear aliphatic diamines produced an unusually high concentration of oligomeric species during synthesis via the solventless protocol. In an effort to minimize the generation of oligomers, synthesis was conducted with the reactants diluted to a concentration of 15 wt% in chloroform, but with paraformaldehyde rather than formalin as is customarily used in solvented benzoxazine synthesis. Prior to large-scale synthesis, reactions were monitored by NMR spectroscopy in order to optimize the reflux times for each diamine-based monomer. The reaction times increase as a function of diamine chain length and were chosen such that the synthesis reached near complete amine consumption without allowing significant oligomeric species to develop.

3.2. NMR analysis of monomer

The structure of the linear aliphatic diamine-based benzoxazines was confirmed by both NMR and FTIR spectroscopies. The proton NMR spectra for the series of diamine-based benzoxazines are shown in Fig. 2. Each spectrum shows two peaks, centered at approximately 4.0 and 4.9 ppm, which are consistent with the formation of a benzoxazine ring. The Mannich bridge protons of open oxazine rings are typically located at approximately 3.7 ppm, which was confirmed for these compounds in other work [23]. The absence of any proton peaks in this region indicates that the alcohol washes were successful in separating any oligomeric species from the monomers. Integration analysis of the proton peaks shows the closed-ring content of each compound to be better than 98%. Making sure that the monomer synthesized has high purity is especially important for polymerization kinetic study as the typical phenolic impurity as either the original phenolic compound used for the synthesis or polybenzoxazine oligomers, both act as the cationic initiators for benzoxazine polymerization. Thus, the accuracy of the study is adversely affected.

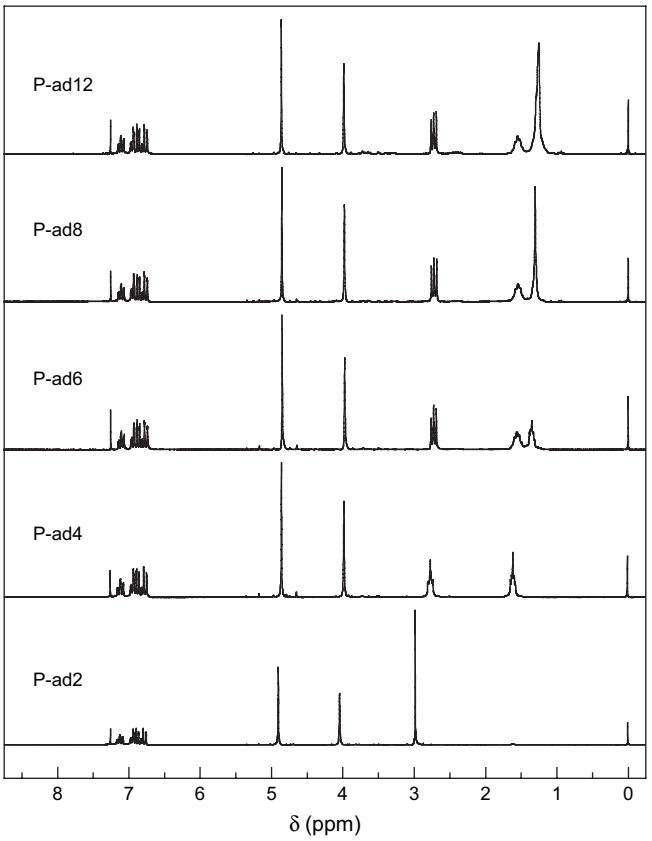


Fig. 2. Proton NMR spectra of the aliphatic diamine-based series of benzoxazines.

The ^{13}C NMR spectra for the series of aliphatic diamine-based benzoxazines are presented in Fig. 3. Although not shown, attached proton test (APT) spectra were also obtained in order to facilitate the ^{13}C peak assignments summarized in Table 1.

3.3. Infrared analysis of monomer

As would be expected, the infrared spectra of the benzoxazine monomers are nearly identical for all of the different diamine chain lengths. There are a number of infrared bands in the spectra, which can be used to verify the formation of oxazine rings in each monomer. While not shown, the presence of the benzoxazine ring aromatic ether is confirmed using absorbance peaks at 1033 and 1223 cm^{-1}, due to the C–O–C symmetric and asymmetric stretching modes, respectively [24]. The absorbances at 752 cm^{-1} were used to show the presence of the expected *ortho*-substituted benzene rings [25], while the peaks at 923 and 934 cm^{-1} are used to confirm the presence of benzene with an attached oxazine ring. Also noteworthy is the complete lack of bands from free or

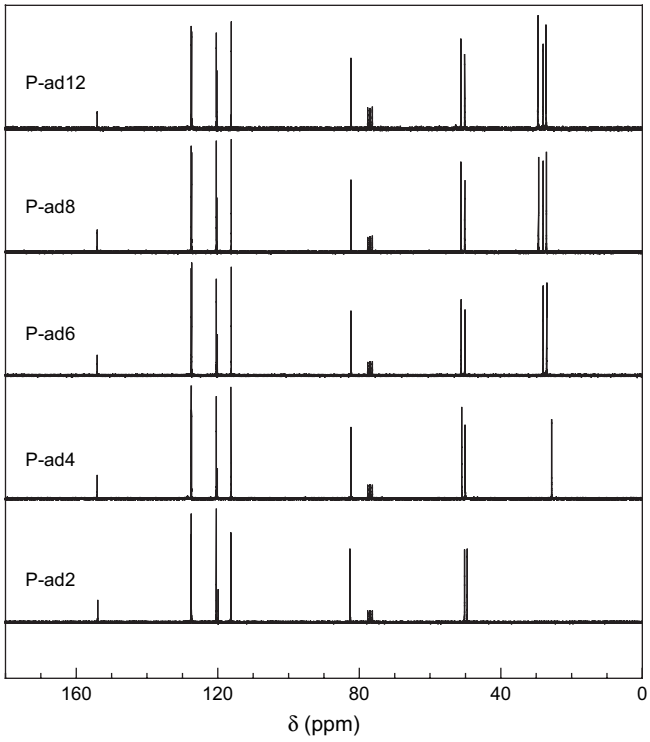


Fig. 3. ^{13}C NMR spectra of the aliphatic diamine-based series of benzoxazines.

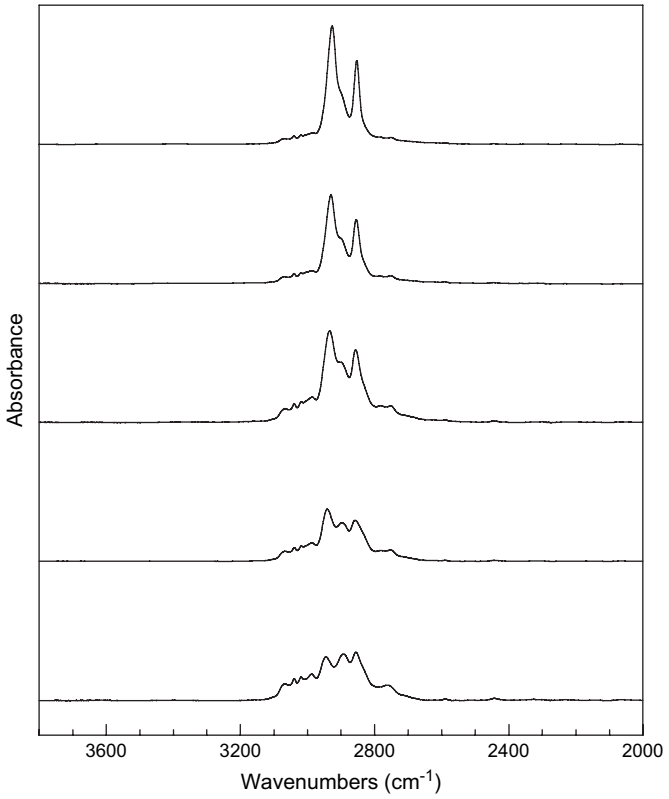
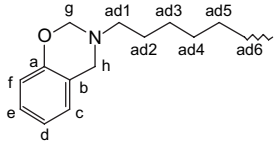


Fig. 4. Fourier transform infrared spectra of the aliphatic diamine-based benzoxazine series of monomers plotted over the hydroxyl region (3800–2000 cm^{-1}).

Table 1
Peak assignments from the ^{13}C analysis of the linear aliphatic diamine-based benzoxazine monomers



Carbon	C2m	C4m	C6m	C8m	C12m
ad2	–	25.68	27.05	27.12	27.20
ad3	–	–	28.00	28.06	28.11
ad4	–	–	–	29.41	29.47
ad5	–	–	–	–	29.52
ad6	–	–	–	–	29.54
h	50.31	50.12	50.17	50.20	50.22
ad1	49.51	51.09	51.22	51.31	51.36
$CDCl_3$	77.00	77.00	77.00	77.00	77.00
g	82.64	82.42	82.37	82.38	82.39
f	116.36	116.30	116.27	116.28	116.28
b	119.91	120.16	120.19	120.24	120.26
d	120.51	120.41	120.38	120.37	120.36
e	127.50	127.49	127.47	127.47	127.48
c	127.68	127.60	127.56	127.55	127.55
a	154.06	154.15	154.14	154.17	154.18

hydrogen-bonded hydroxyl groups in the higher frequency region of each spectrum shown in Fig. 4. The absence of hydroxyl groups shows that the reaction optimization and purification has successfully eliminated any unreacted phenol and oligomeric species.

3.4. Kinetics of polymerization

The effect of diamine chain length on the polymerization kinetics of this benzoxazine monomer series was also investigated through infrared spectroscopy. Polymerization of the monomer at 180 °C was continuously monitored using a heated transmission cell placed in the spectrometer. The benzoxazine-related absorbance peak located between approximately 875 and 965 cm^{-1} is consumed during the ring-opening polymerization, Fig. 5. Because this absorbance band does not have any significant overlapping peaks, the fraction of benzoxazine rings that have been opened during polymerization can be calculated from the change in area of this ring mode. Without an added initiator, a benzoxazine monomer relies on the thermal activation of the oxazine ring to produce the phenolic species required to activate the autocatalytic polymerization reaction. If it is assumed that Mannich bridge formation immediately follows soon after the ring opening [26], then the area changes of this absorbance band can be used as an indicator of the extent of reaction. Although this assumption is not entirely correct as there is a time lag between the ring opening and polymerization, it is nonetheless acceptable as the first approximation for the purpose of the current study. The fraction of this benzoxazine ring mode consumed as a function of reaction time at 180 °C is presented in Fig. 6 for each of the diamine-based monomers. P-ad2, the diamine monomer with the shortest aliphatic chain, consumes its benzoxazine rings most quickly and reaches 50% conversion in just over 5 min. To reach this same

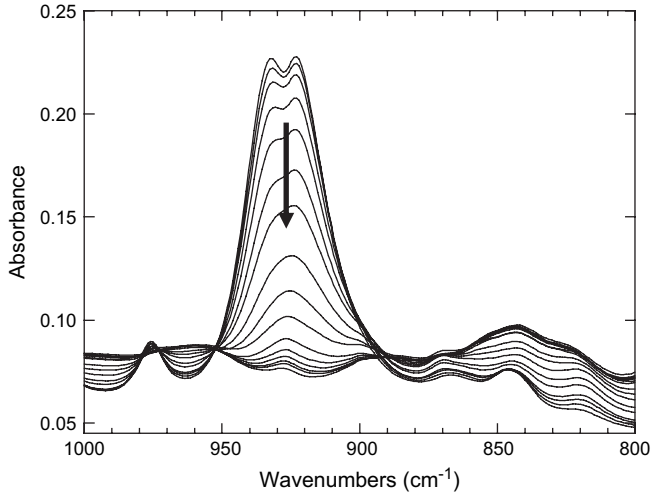


Fig. 5. Disappearance of the benzoxazine-related infrared absorbance peak located between 875 and 965 cm^{-1} during the ring-opening polymerization of P-ad12 at 180 °C.

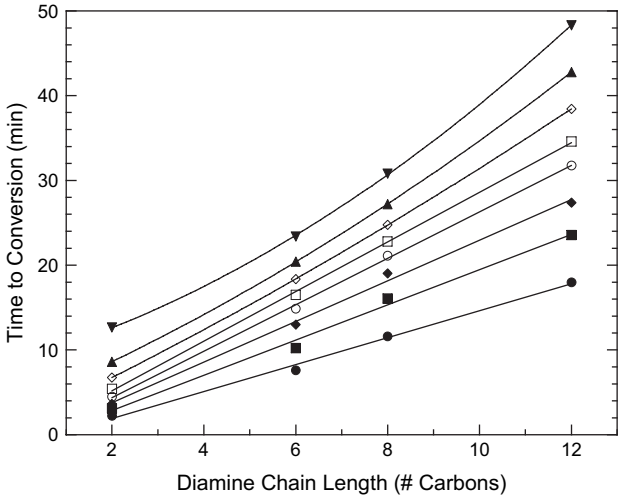


Fig. 7. Time of reaction to reach set conversion as a function of diamine chain length for conversions of 10% (●), 20% (■), 30% (◆), 40% (○), 50% (□), 60% (◇), 70% (▲), and 80% (▼).

conversion, P-ad4, P-ad6, P-ad8, and P-ad12 require approximately 22.7, 16.5, 22.8, and 34.6 min, respectively. Aside from the anomalous behavior of P-ad4, the rate of polymerization seems to be almost linearly related to the length of the aliphatic diamine chain on which each monomer is based. This can be clearly observed in Fig. 7, which plots the time to a given conversion as a function of the number of carbons in each diamine chain. Thus, it appears in general that the thermal stability of the benzoxazine ring is directly related to and increases with the length of the aliphatic diamine chain.

3.5. Infrared analysis of polymer

An infrared spectrum was also obtained for each of the cured diamine-based polybenzoxazines that were formed during the kinetic experiments. For each polymer, the absorbance bands associated with the closed oxazine ring have completely disappeared, including those contributed from the aromatic ether at 1033 and 1223 cm^{-1}, as well as those characteristic of the benzoxazine structure at 923 cm^{-1} (not shown). A small amount of Shiff's base is seen at around 1650 cm^{-1}.

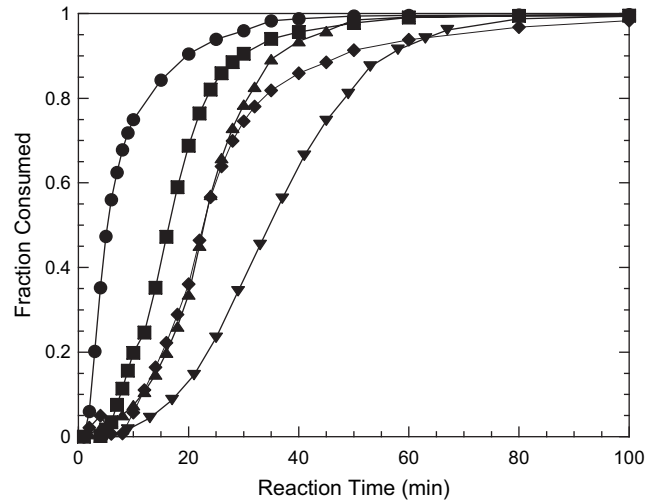


Fig. 6. Consumption of the benzoxazine ring mode located between 965 and 875 cm^{-1} during polymerization at 180 °C for the P-ad2 (●), P-ad4 (◆), P-ad6 (■), P-ad8 (▲), and P-ad12 (▼) monomers.

During the polymerization of benzoxazines, a phenolic hydroxyl group is theoretically produced for every oxazine ring that is opened. Previous research has shown that hydrogen bonding of this hydroxyl group plays an important role in the network structure of polybenzoxazines and may contribute to many of their physical and mechanical properties [10,27]. The hydroxyl region for each of the diamine-based polybenzoxazines is shown in Fig. 8. Absent from each polymer spectrum is the vibrational peak for free or relatively free hydroxyl groups which have been shown to absorb above 3600 cm^{-1} in model benzoxazine dimers [27]. This suggests that all of the phenolic hydroxyl groups are involved in some form of intra- or intermolecular hydrogen bonding. The spectral similarities between the different polymers across this region indicate that there is little variation in the form or type of hydrogen bonding that occurs in each polymer network. The strongest hydrogen-bonded hydroxyl band in these materials is located at approximately 3180 cm^{-1} and is consistent with −OH···N intramolecular hydrogen bonding in the Mannich bridge. There is also a much weaker intramolecular absorption band appearing near 3530 cm^{-1}, which is assigned to −OH···π hydrogen bonding [28]. Unlike polybenzoxazines based on a bisphenol and monofunctional aliphatic amine [29], the aliphatic diamine-based series of polymers all possess a hydrogen-bonded hydroxyl peak near 3310 cm^{-1} and thus have some degree of −OH···O intermolecular hydrogen bonding. A similar absorbance band is seen in bisphenol/aromatic amine-based polybenzoxazines as well as methyl substituted phenols themselves.

3.6. Differential scanning calorimetry

The thermally activated cure behavior of the aliphatic diamine-based benzoxazine series was also studied by

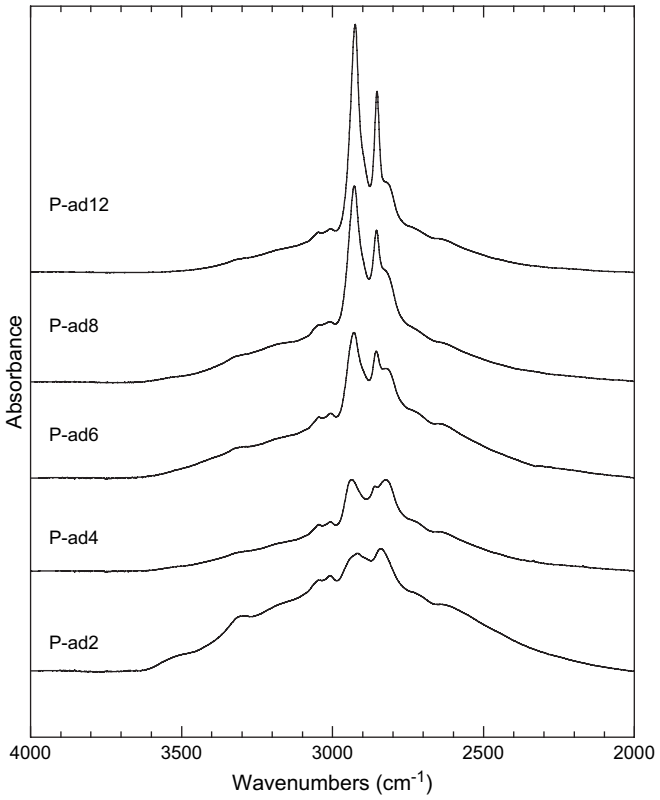


Fig. 8. Fourier transform infrared spectra of the aliphatic diamine-based benzoxazine series of monomers plotted over the hydroxyl region (3800–2000 cm^{-1}).

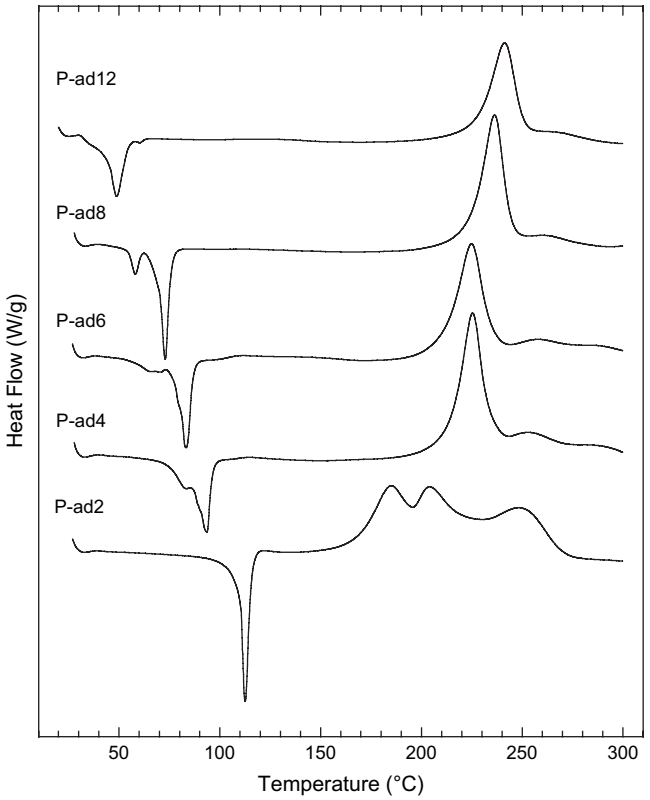


Fig. 9. Nonisothermal DSC thermograms of the aliphatic diamine-based series of benzoxazine monomers cured in a nitrogen environment.

differential scanning calorimetry and is summarized in Table 2. In Fig. 9, the nonisothermal DSC thermograms are plotted for each of the monomers. As is demonstrated in Fig. 10, the peak positions of the melting point endotherms decrease almost linearly as a function of diamine chain length, from a high of 112 °C for the shortest chain ($n = 2$) diamine-based material to a low of 49 °C for the monomer with the longest diamine chain ($n = 12$).

Upon inspection of the monomer polymerization exotherms, it appears that their position generally seems to increase with the length of the aliphatic diamine chain. However, the shortest chain monomer, P-ad2, is unique in that its exotherm is comprised of three separate processes, centered at 185, 205, and 250 °C. This behavior is often observed when the monomer contains phenolic impurities such as oligomers and an initial phenolic compound used for the monomer synthesis. However, as can be seen in Figs. 2 and 3, the purity of this monomer, P-ad2, is the highest of all the benzoxazine monomers studied in this work. Thus, initiation by impurities is unlikely the cause of this anomaly. The first exothermic peak is remarkable in that it may be the lowest temperature ever observed for the uncatalyzed polymerization exotherm of a difunctional benzoxazine and is significantly lower than bisphenol-based benzoxazines, which typically have a peak exotherm in the range from 225 to 250 °C. It will be shown in the later section on thermal stability that degradation is most likely responsible for the highest temperature exothermic peak at 250 °C in the P-ad2 monomer. Thus, polymerization of P-ad2 seems to occur by a dual mode process. It is hypothesized that the very short ethane linkage separating the amine functionalities of the P-ad2 monomer may allow steric hindrance or other unique conformational factors and interactions to destabilize the oxazine rings. This destabilization decreases

Table 2
Results of the nonisothermal differential scanning calorimetry cure analysis of the linear aliphatic diamine-based benzoxazine monomers

	P-ad2	P-ad4	P-ad6	P-ad8	P-ad12
Melting temperature (°C)	112	94	83	73	49
Exotherm position (°C)	185	225	225	236	241
Total exotherm (J/g)	575	418	367	288	255
Cure exotherm (J/g)	444	335	292	272	229
Deg. exotherm (J/g)	131	82.4	75.9	16.0	26.3
Molecular weight (g/mol)	296.36	324.42	352.47	380.52	436.63
Heat of polymerization (kJ/mol)	132	109	103	104	100

The exotherm position is taken at the maximum.

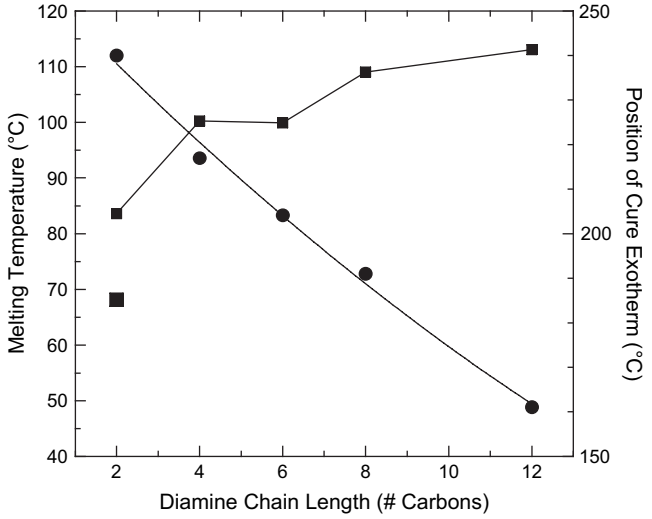


Fig. 10. Melting temperature (●) of the benzoxazine monomers and position of the peak in cure exotherm (■) as a function of diamine chain length.

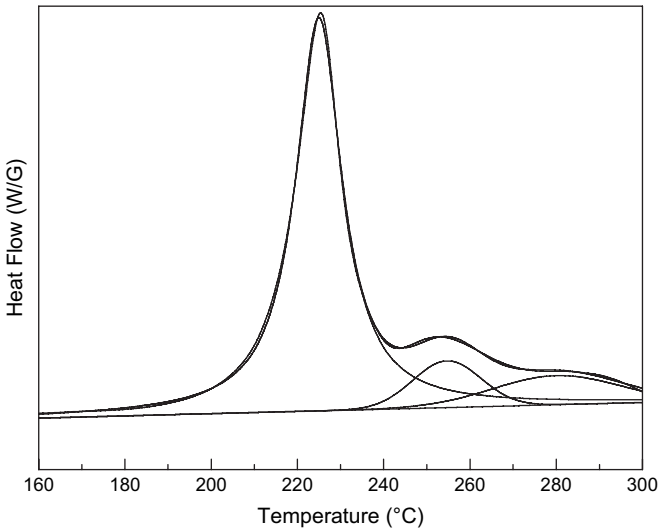


Fig. 11. Curve fitting of the P-ad4 cure exotherm includes original thermogram, modeled peaks, and fitted curve.

after the first benzoxazine ring has opened, thus increasing the temperature required for thermal activation of the monomer's second oxazine ring.

The diamine monomers with butane or longer linkages have further separated oxazine rings, and each exhibit only a single polymerization exotherm. The small shoulders at or above 250 °C are again attributed to degradation rather than polymerization. The peak exotherm for the P-ad4 monomer seems to be at a higher temperature and thus has more thermally stable oxazine rings than the general trend of this monomer series would indicate. This is consistent with the infrared kinetic results in which this monomer consumed its oxazine rings at a slower rate than would be expected.

Analysis of the heat of reaction during polymerization for the aliphatic diamine series of monomers is complicated by the overlap occurring between the curing and degradation peaks in the DSC thermograms. However, the heat of polymerization can be extracted from the combined curing and degradation exotherm through careful peak fitting analysis, an example of which is shown in Fig. 11 for the P-ad4 monomer. In this case, the exotherm is modeled (Grams/32) with three mixed Gaussian–Lorentzian peaks, one at 225 °C for polymerization and two for degradation, at 255 and 280 °C. The area of the fitted polymerization peak, 57.0 W °C/g, is divided by the actual heating rate, 0.170 °C/sec, to obtain the extracted heat of reaction for the curing process, 335 J/g. The heat of reaction for polymerization calculated from the fitted exotherm of each monomer in this benzoxazine series is presented in Fig. 12 as a function of the aliphatic diamine chain length. This curing exotherm is highest, at 444 J/g, for the monomer with the shortest aliphatic chain, P-ad2, and continuously decreases with longer aliphatic chains to 229 J/g for P-ad12. This is partly to be expected as the number of oxazine rings per gram also decreases as a function of diamine chain length and thus, for a proper comparison, the cure exotherms must be normalized by the molecular weight to give the heat of polymerization per mole. In this case, P-ad2 still possesses the highest exotherm at 132 kJ/mol, but beyond the ethane linkage, the heat of polymerization is relatively constant, at just above 100 kJ/mol. The curve fitting to DSC thermogram is not a well-established practice as the line contour of each band is not easy to determine. Therefore, the results shown here should only be viewed as qualitative guideline rather than quantitative analysis, although use of curve fitting to thermograms has been discussed in the literature [30]. P-ad2 value deviates from all the other compounds studied. At this time, the molecular reason for this phenomenon is not known.

3.7. Optimization of polymerization

As previously discussed, polymerization of the aliphatic diamine-based series of monomers is overlapped by degradation at higher temperatures. Thus, prior to characterization

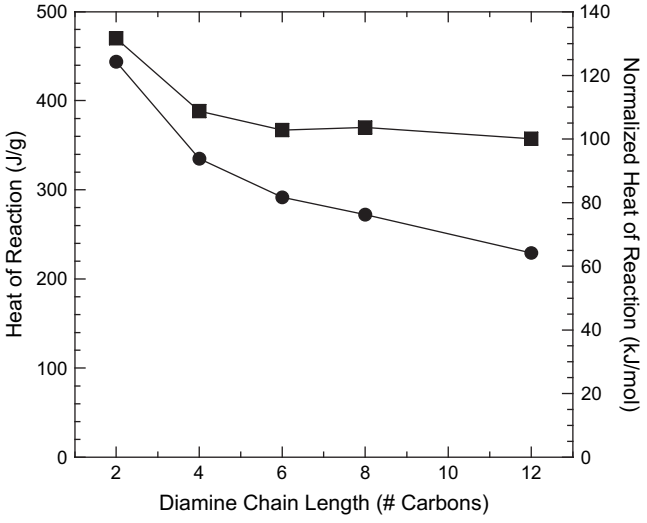


Fig. 12. Heat of reaction (●) and normalized heat of reaction (■) as a function of the number of carbons in the aliphatic diamine chain of the benzoxazine monomers.

Table 3
Summary of the glass transition temperatures determined by DSC for each of the different cure profiles in the optimization of polymerization conditions for the linear aliphatic diamine-based benzoxazines

Cure Profile		P-ad2	P-ad4	P-ad6	P-ad8	P-ad12
Temperature (°C)	Time (h)					
140/160	1/1	140	105	–	–	–
140/160/180	1/1/1	175	162	143	128	93
140/160/180	1/1/2	179	169	157	136	105
140/160/180	1/1/3	174	167	171	135	103
140/160/180/190	1/1/1/1	178	172	164	137	100
140/160/180/190	1/1/1/2	162	160	156	132	105
T_g (max)		179	169	171	137	105

of the polybenzoxazines derived from these monomers, it is important to individually optimize the curing profile for each different compound. This ensures that the materials are not over-cured and that degradation does not negatively influence the mechanical and physical properties of the polymers. Samples for each benzoxazine were polymerized by a number of different cure profiles then scanned by DSC. The glass transition temperatures for each compound and cure profile are summarized in Table 3. All of the benzoxazines, except for the P-ad12 compound, began to degrade beyond 1 h at 190 °C, and thus this should be seen as the upper limit in time and temperature for curing these materials. The profile to be used in curing samples for mechanical and physical testings of each diamine-based polybenzoxazine was selected based on the maximum obtainable glass transition temperature, which will be discussed in later sections. Degradation often leads to increased T_g due to increased degree of crosslinking. However, in this series of polybenzoxazines, it appears chain scission that leads to reduction of T_g is the dominant degradation mode.

3.8. Effect of atmosphere on polymerization

In order to study the effect of atmosphere on the polymerization of aliphatic diamine-based benzoxazine monomers, the nonisothermal DSC experiments were repeated with dry air instead of nitrogen as the cell pressurization and purge gas. As is readily apparent in Fig. 13, the change of atmosphere significantly affects the shape and position of the polymerization exotherms in comparison to the results obtained under a nitrogen purge shown in Fig. 9. The onset of polymerization is shifted to as low as 100 °C while the peaks themselves have significantly broadened with maxima that are shifted to temperatures approximately 15 °C lower. While broad, lower temperature exotherms could be advantageous, the effects of the polymerization atmosphere on the resulting polymer must first be investigated. To do so, P-ad6 was step cured in each atmosphere to a maximum temperature of 180 °C for 3 h in the pressurized DSC cell. A second nonisothermal scan was performed under nitrogen for each polymerized sample. The air atmosphere has very negative effects on the polymer structure, as the glass transition temperature is now only 127 °C, a decrease of more than 40 °C. An explanation is readily apparent after infrared spectroscopic analysis of

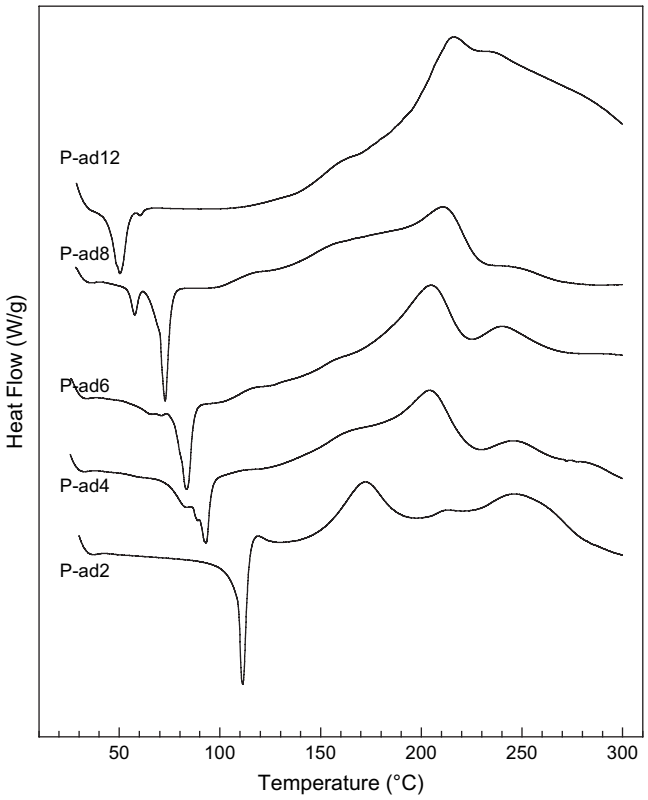


Fig. 13. Nonisothermal DSC thermograms of the aliphatic diamine-based series of benzoxazine monomers cured in a dry air environment.

samples partially cured in each atmosphere. Upon comparing the fingerprint regions of each sample, there are two revealing peaks that appear only for the P-ad6 material cured in the air environment (Fig. 14). These peaks, a carbonyl band at 1675 cm^{-1} and a radial benzene mode (Wilson mode 13) at 1258 cm^{-1}, are consistent with the formation of substituted benzoquinone (SB) which has been identified previously as a product formed by the degradation of bisphenol-based polybenzoxazines after exposure to ultraviolet radiation in an oxidative environment [31]. The formation of substituted benzoquinones during the polymerization of the aliphatic diamine-based monomers could have two detrimental effects on the network structure. First, the *para*-position of the aromatic ring is a potentially reactive crosslinking site during polymerization and would be blocked if an SB were formed. Secondly, a SB would interfere with hydrogen bonding as it turns the hydroxyl group into a carbonyl group that cannot participate in these interactions. Both would be expected to adversely affect the glass transition temperature as well as mechanical properties of cured aliphatic diamine-based polybenzoxazines, although it is probable that the effects would be limited to a thin layer of benzoxazine at the exposed surface.

3.9. P-ad2 as an initiator for polymerization

In addition to the tremendous potential that the linear aliphatic diamine-based series has shown as a viable subclass

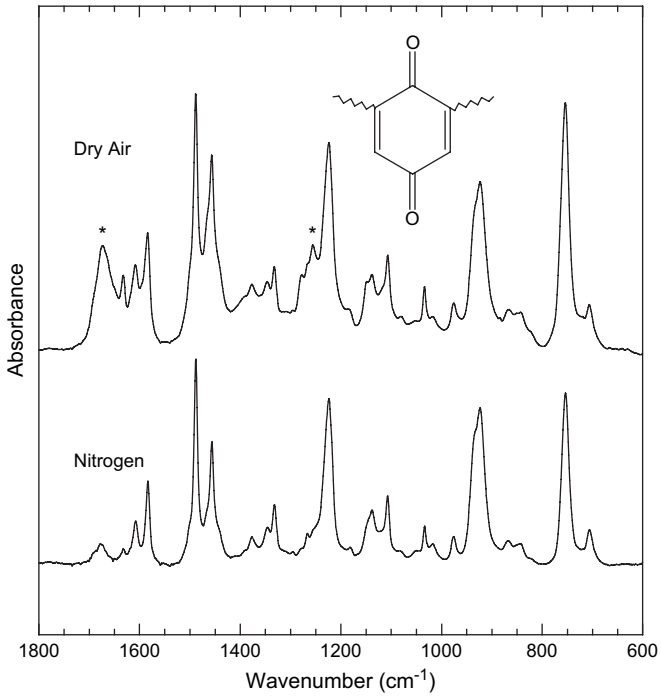


Fig. 14. Comparison of the fingerprint region for the infrared spectra of P-ad6 partially cured in a nitrogen atmosphere (lower) and a dry air environment (upper).

of the polybenzoxazine family, these materials may also find utility as additives to enhance certain characteristics of other benzoxazines that have already been developed. It was shown earlier that P-ad2 has one of the lowest onset temperatures observed to date for the polymerization of a benzoxazine. In an effort to exploit this characteristic, a small amount of P-ad2 monomer was added as a reactive initiator to the most popular bisphenol-based benzoxazine, 6,6′-bis(3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl)isopropane (BA-a), and cured under nitrogen in the DSC. When thermally polymerized without any additives, the onset of polymerization for BA-a does not begin until at least 200 °C, with the exothermic peak centered at 238 °C and a heat of reaction of 285 J/g. However, when 10 wt% P-ad2 is added as a reactive initiator, the onset of polymerization is shifted almost 75 °C lower, the exotherm becomes very broad, and now has a peak that is centered at only 224 °C with a heat of polymerization remains nearly unchanged at 286 J/g. Thus, P-ad2 can quite effectively serve as an initiator for BA-a by significantly lowering the temperature required for polymerization, and would not be expected to have any major adverse effects on the polybenzoxazine since it is reactive and will incorporate directly into the network structure.

4. Conclusions

An investigation into the kinetics of polymerization by infrared spectroscopy reveals that rate of polymerization is inversely proportional to the aliphatic diamine chain length. All of the phenolic hydroxyl groups produced by thermally activated polymerization of the diamine benzoxazines were shown to be hydrogen bonded, with the majority involved in intramolecular bonding but some hydroxyls participating in intermolecular bonds. The aliphatic diamine-based polybenzoxazines have high glass transition temperatures, above 170 °C for the shortest three diamines, before decreasing with further increases in the diamine chain length.

The linear aliphatic diamine-based series of benzoxazine monomers exhibited a significant sensitivity to the atmosphere of the polymerization environment. Polymerization in dry air at an elevated pressure allowed oxidative effects consistent with the formation of a substituted benzoquinone structure to negatively influence the polybenzoxazine properties.

Differential scanning calorimetry determined that the melting points of these benzoxazines decrease as a function of diamine chain length, while the temperature of the peak polymerization exotherm increases for longer aliphatic diamines. The heat of polymerization, normalized to molecular weight, was largely independent of diamine chain length, and was relatively constant at just above 100 kJ/mol. A notable exception is the monomer based on the shortest aliphatic diamine, ethylene diamine. This sub-180 °C onset of polymerization for P-ad2 is lower than any other benzoxazine exotherm reported to date and allows the monomer to be used as a reactive initiator in other benzoxazine systems. The molecular reason for this is not known at this time and further detailed investigation is needed.

Acknowledgment

The authors gratefully acknowledge the financial support of Sekisui Integrated Research.

References

[1] Lui JP, Ishida H. Polym Polym Compos 2002;10:191.
[2] Agag T, Takeichi T. Macromolecules 2001;34:7257.
[3] Kimura H, Matsumoto A, Sugito H, Hasegawa K, Ohtsuka K, Fukuda A. J Appl Polym Sci 2001;79:555.
[4] Brunovska Z, Lyon R, Ishida H. Thermochim Acta 2000;357:195.
[5] Ishida H, Sanders DP. J Polym Sci Part B Polym Phys 2000;38:3289.
[6] Kim HJ, Brunovska Z, Ishida H. Polymer 1999;40:6565.
[7] Kimura H, Matsumoto A, Hasegawa K, Fukuda A. J Appl Polym Sci 1999;72:1551.
[8] Kimura H, Murata Y, Matsumoto A, Hasegawa K, Ohtsuka K, Fukuda A. J Appl Polym Sci 1999;74:2266.
[9] Shen SB, Ishida H. J Polym Sci Part B Polym Phys 1999;37:3257.
[10] Ishida H, Allen DJ. J Polym Sci Part B Polym Phys 1996;34:1019.
[11] Brunovkska Z, Lui JP, Ishida H. Macromol Chem Phys 1999;200:1745.
[12] Ning X, Ishida H. J Polym Sci Part A Polym Chem 1994;32:1121.
[13] Reiss G, Schwob JM, Guth G, Roche M, Lande B. In: Culbertson BM, McGrath JE, editors. Advances in polymer synthesis. New York: Plenum Press; 1985. p. 27–49.
[14] Allen DJ, Ishida H. J Appl Polym Sci 2006;101:2798.
[15] Li S, Wang L. J Appl Polym Sci 2006;99:1359.
[16] Jang J, Seo D. J Appl Polym Sci 1998;67:1.
[17] Jang J, Yang H. Compos Sci Technol 2000;60:457.
[18] Ishida H, Lee YH. Polym Polym Compos 2001;9:121.
[19] Ishida H, Allen DJ. Polymer 1996;37:4487.
[20] Ishida H, Lee YH. Polymer 2001;42:6971.

[21] Takeichi T, Guo Y, Agag T. J Polym Sci Part A Polym Chem 2000;38:4165.
[22] Ishida H. US Patent 5,543,516; 1996.
[23] Allen DJ, Ishida H, submitted for publication.
[24] Dunkers J, Ishida H. Spectrochim Acta 1995;51A:1061.
[25] Colthup NB, Daly LH, Wiberly SE. Introduction to infrared and Raman spectroscopy. 3rd ed. New York: Academic; 1990.
[26] Dunkers J, Ishida H. J Polym Sci Part A Polym Chem 1999;37:1913.
[27] Kim HD, Ishida H. J Phys Chem A 2002;106:3271.
[28] Cairns T, Eglinton G. J Am Chem Soc 1965;5906.
[29] Kim HD, Ishida H. Macromolecules 2003;36:8320.
[30] Rotter G, Ishida H. Macromolecules 1992;25:2170.
[31] Macko J, Ishida H. J Polym Sci Part B Polym Phys 2000;38:2687.