Resorcinol-Based Benzoxazine with Low Polymerization Temperature

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ABSTRACT: The industrial applications of benzoxazines are limited due to their high curing temperatures. This drawback can be overcome by more reactive precursor compared to conventional benzoxazines or by application of efficient initiators. We report the synthesis of a new resorcinol-based benzoxazine and its cationic polymerization with thermolatent super acids, namely organic sulfonium hexafluoroantimonates. This combination of a reactive precursor and an efficient initiator results in a curing temperature below 100 °C (differential scanning calorimetry onset) which is up to now one of the lowest polymerization temperatures for benzoxazine systems. Furthermore, the thermal stability of the formed polybenzoxazine has not been influenced by the applied initiators. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1693–1699

KEYWORDS: benzoxazine; cationic polymerization; initiators; latent initiator; resorcinol-based benzoxazine; ring-opening polymerization; thermosets

INTRODUCTION Polybenzoxazines are phenolic-type resins resulting from polymerization of 1,3-benzoxazine precursors.[1] These thermosets combine the advantages of epoxy resins like design flexibility and mechanical behavior and both thermal and flame retarded properties of phenolic resins.[2] Furthermore, polybenzoxazines show nearly no volume shrinkage while curing, they do not release any byproducts during reaction, exhibit high glass transition temperatures T_g and high char yield. Additionally, benzoxazines do adsorb water only in a low amount and at last they do not need any initiators for polymerization reaction.[1,3,4] On the other hand, polybenzoxazines exhibit some shortcomings like brittleness and high curing temperatures.[1,5] In order to overcome the drawback of high polymerization temperature, two ways were examined in the past: First, the development of a more reactive benzoxazine precursor and, second, the catalytic acceleration of the polymerization reaction.

In 1944, Holly and Cope synthesized the first benzoxazines by condensation reaction of phenol, formaldehyde and a primary amine.[6] Five years later, Burke et al. demonstrated that benzoxazines react preferentially by their free ortho-position.[7] Furthermore, benzoxazines have been functionalized by reactive groups like acetylene,[8] allyl group,[9] propagyl group,[10] nitrile,[11] maleimide,[12] coumarin,[13] epoxy group,[14] cardanol,[15] hydroxymethyl group,[16] or norbonane.[12] Such functional groups modify the mechanical and thermal behavior but they do not decrease the polymerization temperature of the benzoxazine units themselves, even though they react to prepolymers at lower temperatures by polymerizable non-oxazine groups. Some examples for known benzoxazines and their self-polymerization temperatures T_c (measured by differential scanning calorimetry, DSC) are phenol/aniline-based benzoxazine with T_c of 263 °C, *p*-cresol/aniline-based benzoxazine with T_c of 269 °C, 1-naphthol/aniline-based benzoxazine with T_c of 156 °C (broad DSC signal), and bisphenol-A/aniline-based benzoxazine with T_c of 249 °C.[1,17] Except from the 1-naphthol-based benzoxazine, the curing temperatures of most benzoxazines are very high.

Wang and Ishida published investigations on different cationic ring-opening mechanisms, which result in oxonium and iminium ions as intermediates because of the basicity of the oxazin-oxygen and -nitrogen atoms.[18,19] The driving force of benzoxazine ring-opening reaction is proposed to be the ring stress of the distorted oxazine ring structure.[4] Wang and Ishida demonstrated that different initiators lead to two different structures as a consequence of different mechanisms.[19] These structures are known as Mannich base phenoxy-type polybenzoxazine (type I) and as Mannich base phenolic-type polybenzoxazine (type II) which are able to rearrange.[20] Several effective and even efficient catalysts and initiators were developed to reduce the curing temperature of benzoxazines. Initiators are usually Lewis acids like phosphorus pentachloride, titanium chloride, and aluminum chloride,[18] carboxylic acids like trifluoroacetic acid and sebacic acid,[21] alcohols

like *p*-cresol and 2-methylresorcinol,[21,22] thiols like benzylthiol,[23] metal complexes like acetylacetonato-complexes with iron, manganese, or cobalt,[24] sulfonates like *p*-toluenesulfonate,[17] salts like lithium iodide,[5,25] and photolatent onium salts like diphenyliodonium and triphenylsulfonium salts.[26,27] Examples for really efficient known benzoxazine/initiator systems and their respective curing temperatures (measured by DSC) are BA-a/PCl_5 with T_c of 122 °C, *p*C-a/LiI with T_c of 197 °C, *p*C-a/$Zn(OTf)_2$ with T_c of 199 °C, and *p*C-a/*p*-toluenesulfonates with T_c of 100–120 °C (not measured by DSC).[5,17,18]

To the best of our knowledge, onium salts have not been applied for thermal benzoxazine polymerization up to now. Photo- or thermolatent initiators that are known for epoxide polymerization react by a cationic mechanism and, for this reason, they seem to be feasible for initiating benzoxazine polymerization.[28–33] Besides, such initiators can be applied in formulations with long shelf-life. Thermolatent initiators like *p*-methoxybenzyl tetrahydrothiophenium hexafluoroantimonate (**3**) and benzyl tetrahydrothiophenium hexafluoroantimonat (**4**) form a super acid or a carbocation during thermal or photochemical decomposition, respectively. These two initiators (**3**) and (**4**) show different activation temperatures for divinyl ether and in other words different reactivity according to their structures.[34] They may also show different reactivity toward benzoxazines. Recently, Oie et al. demonstrated a new approach to form polybenzoxazines due to ring-opening addition.[22,35] This reaction of a benzoxazine ring with 2-methylresorcinol occurs at ambient conditions and is therefore a promising concept. In this case, the 2-methylresorcinol is both initiator (protonation of benzoxazine by phenolic hydroxyl group) and also monomer for addition reaction.

In this work, we synthesized and characterized a new reactive resorcinol-based benzoxazine R-a (**1**). We investigated the polymerization reaction of this new benzoxazine (**1**) in comparison to an established bisphenol A-based benzoxazine BA-a (**2**) as well as the influence of thermolatent initiators (**3**) and (**4**) on both benzoxazines (**1**) and (**2**).

EXPERIMENTAL

Materials

All chemicals were used as received from commercial suppliers. Toluene (99.8%), petroleum ether (p.a., 40–60 °C), formaldehyde (37 wt % in water, 10–15% methanol as stabilizer), aniline, and resorcinol (99%) were purchased from Sigma Aldrich (Schnelldorf, Germany). 6,6'-(Propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazine) (Araldite® MT 35600, BA-a (**2**)) was obtained from Huntsman (Everberg, Belgium). The latent initiators *p*-methoxybenzyl tetrahydrothiophenium hexafluoroantimonate (**3**) and benzyl tetrahydrothiophenium hexafluoroantimonat (**4**) were prepared according to the literature.[28,36]

Physicochemical Characterization

Infrared spectra were obtained in attenuated total reflection (ATR) with a Bruker Equinox 55 FTIR-spectrometer equipped with a Golden Gate cell with a resolution of 4 cm^{-1} (32 scans). ^1H NMR, ^{13}C NMR, HH-COSY, HSQC, and HMBC spectra were recorded with a Bruker AVANCE NB 360 spectrometer. Tetramethylsilane was used as external standard. The spectra were measured in $CDCl_3$ at room temperature. Mass spectra were measured with a Finnigan MAT 95 using electron-induced ionization at 200 °C with an ionization energy of 70 eV. The samples were injected with an indirect inlet system. DSC was carried out in a sealed pan with DSC 2920 Modulated from TA Instruments in a temperature range from 20 to 300 °C with a heating rate of 10 K/min. Thermogravimetric analysis (TGA) was carried out with a Q5000 from TA Instruments. The measurements were performed under nitrogen flow, between 20 and 600 °C, with a heating rate of 10 K min^{-1}. Elementary analysis (EA) was measured by Microanalytical Laboratory Pascher (Remagen, Germany).

Synthesis

Resorcinol-Based Benzoxazine Isomer Mixture (R-a) Consisting of 3,9-Diphenyl-3,4,9,10-tetrahydro-2H,8H-[1,3]oxazino-[6,5-f][1,3]benzoxazine (I) and 3,7-Diphenyl-3,4,7,8-tetrahydro-2H,6H-[1,3]oxazino-[5,6-g][1,3]benzoxazine (II) (1)

Formaldehyde [3 mL (40 mmol)] were dissolved in 5 mL of 1,4-dioxane. Afterward, 1.85 mL (20 mmol) of aniline was slowly dropped into the solution under stirring. The mixture was stirred for 30 min until a white solid precipitated. Thereafter, the mixture was started to reflux to dissolve the precipitate. Subsequently, a solution of 1.10 g (10 mmol) resorcinol in 2.5 mL of 1,4-dioxane was slowly added. Then, the mixture was refluxed for additional 60 min. The solvent was removed under vacuum (10^{-2} mbar) with a successive temperature rise up to 80 °C (the viscosity increases rapidly). The obtained yellow, transparent solid was further purified by refluxing with a mixture of 20 mL diethyl ether and 4 mL toluene. After cooling to 20 °C the liquid phase was separated from the precipitated residue. The neat product was dissolved in the liquid phase. After the removal of the solvent and drying under vacuum (10^{-2} mbar), we obtained a white crystalline solid with a yield of 13%, which consisted of the two isomers (I) and (II) in a molar ratio of 1:0.14 as determined by different NMR experiments.

NMR *(360 MHz, $CDCl_3$)*

See Table 1; EIMS [m/z (%)]: 344 [M^+], 239, 105, 77. IR (ATR): $\nu = 1595$, 1579, and 1492 (s) $\nu_{C=C}$ (aromatic), 1252 and 1043 (s) $\nu_{aryl\text{-}O}$ ($C_{aromatic}$-O-C), 1151 (m) $\nu_{C\text{-}N}$ (C-N-C), 925 (s) $\delta_{C\text{-}H}$ (1,2,4,5-tetrasubstituted aromatics), 867 (m) $\delta_{C\text{-}H}$ (1,2,4,5-tetrasubstituted aromatics), 809 cm^{-1} (m) $\delta_{C\text{-}H}$ (1,2,3,4-tetrasubstituted aromatics). EA: Calcd for $C_{22}H_{20}N_2O_2$: C 76.72, H 5.85, N 8.13, O 9.29; found: C 76.46, H 5.84, N 8.18, O 9.57.

Polymerization of R-a (1)

The polymerization of the resorcinol-based benzoxazine (**1**) was investigated both (a) with one weight percent of the initiators (**3**) and (**4**) and (b) without initiator. In case of (a),

TABLE 1 ^{1}H and ^{13}C NMR Signals of Isomeric R-a (**1**) and Its Structure Elements

Asymmetric Isomer (I)				Symmetric Isomer (II)			
Numbering/Structure		^{13}C, δ (ppm)	^{1}H, δ (ppm)	Numbering/ Structure		^{13}C, δ (ppm)	^{1}H, δ (ppm)
2	O-CH_2	79.5	5.41	2	O-CH_2	79.2	5.35
4	N-CH_2	49.9	4.59	4	N-CH_2	49.9	4.58
4a	=C_{aryl}	112.1	–	4a	=C_{aryl}	113.5	–
5	=CH	125.0	6.81	5	=CH	124.2	6.67
6	=CH	109.0	6.44	10	=CH	104.5	6.33
8	O-CH_2	78.9	5.33	10a	=C_{aryl}-O	153.5	–
10	N-CH_2	46.0	4.56	11	N-C_{aryl}	148.1	–
10a	=C_{aryl}	109.2	–	12	=CH	~118	~7.14
10b	=C_{aryl}-O	150.8	–	13	=CH	~129	~7.31
11	N-C_{aryl}	148.1	–	14	=CH	~121	~6.98
12/18	=CH	118.1/117.8	7.14				
13/19	=CH	129.0/128.9	~7.3				
14/20	=CH	121.2/121.0	6.98/6.96				
17	N-C_{aryl}	148.3	–				

the R-a (**1**) was mixed together with the initiator by a pestle. The resorcinol-based benzoxazine R-a (**1**) was polymerized for 24 h in a preheated oven at 120 °C (heating profile A). R-a (**1**) was also polymerized in another approach for 2 h at 180 °C and additionally for 2 h at 200 °C (heating profile B) for comparability to the commercial benzoxazine (**2**). We obtained a red brown transparent solid in all six cases.

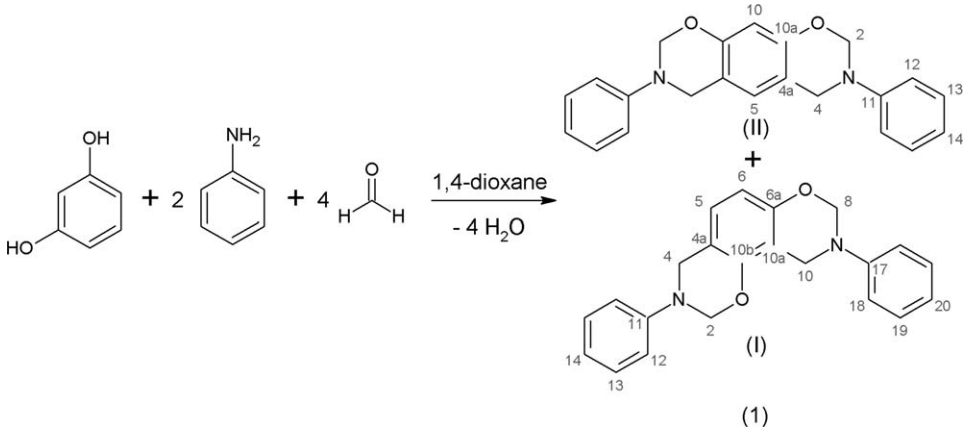
Polymerization of BA-a (2)

The polymerization of BA-a (**2**) was investigated both (a) with the initiators (**3**) and (**4**) and (b) without initiator. In case of (a), the benzoxazine (**2**) was first pestled together with one weight percent initiator. The polymerization was carried out for both procedures (a) and (b) on the one hand for 24 h at 120 °C (heating profile A) and on the other hand according to Huntsman (heating profile B).[37] The polymerization was investigated in a preheated oven. We obtained a deep red transparent solid in case of polymerization according to heating profile B.

RESULTS AND DISCUSSION

Synthesis of Resorcinol-Based Benzoxazine R-a (1)

A new resorcinol-based benzoxazine R-a (**1**) was prepared by reaction of resorcinol with aniline and formaldehyde in a molar ratio of 1:2:4 as can be seen in Scheme 1. A separation of the asymmetric isomer (I) and the symmetric isomer (II) is not necessary for polymerization experiments; thus, it has not been carried out yet. Nevertheless, the isomeric mixture of R-a (**1**) was completely characterized by standard methods like infrared spectroscopy, NMR spectroscopy, EA, and mass spectrometry. The IR spectrum shows all



SCHEME 1 Synthesis of the resorcinol-based benzoxazine R-a (**1**) by reaction of resorcinol with aniline and formaldehyde in a molar ratio of 1:2:4. The numbers (I) and (II) of R-a (**1**) denote the asymmetric and symmetric isomers, respectively. The numberings of the C-atoms in the structure of both isomers refer to the NMR signals, which are listed in Table 1.

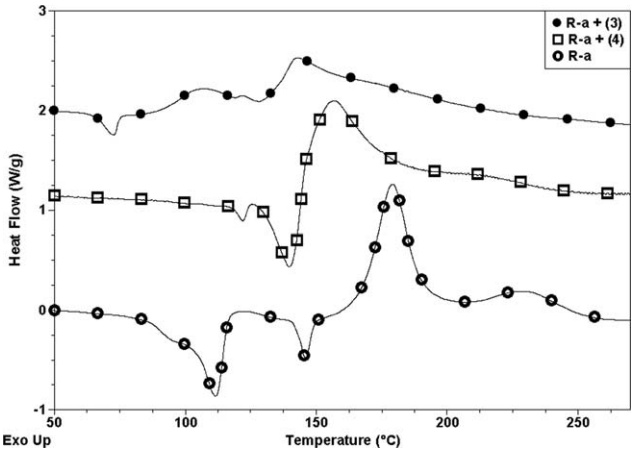


FIGURE 1 DSC thermogram of the polymerization of resorcinol-based benzoxazine R-a (**1**) without initiator and also in presence of both latent initiators (**3**) and (**4**).

significant oxazine ring signals at 1043 cm^{-1}(aryl-O), 1252 cm^{-1} (aryl-O), and 1151 cm^{-1} (C-N-C). In addition, the infrared signals at 925 and 867 cm^{-1} belong to a 1,2,4,5-tetrasubstituted aromatic ring whereas the signal at 809 cm^{-1} indicates a 1,2,3,4-tetrasubstitution which are both characteristic for the isomers (I) and (II). Two-dimensional NMR confirms clearly the formation of isomeric R-a (**1**) as can be seen in Table 1. All C- and H-atoms are assigned to a NMR-signal by measuring ^{1}H NMR, ^{13}C NMR, HH-COSY, HSQC, and HMBC spectra. The resulting two isomeric structures (I) and (II) have a ratio of approximately 7:1 as analyzed by the aromatic ring proton integrals. Furthermore, mass spectrometry reveals typical fragments at m/z 77, 105, and 239. A molecular radical cation at m/z of 344 corresponds to the theoretical mass of R-a (**1**). At last, EA shows that the resorcinol-based benzoxazine R-a (**1**) is pure and that its molecular composition corresponds to the theoretical one. DSC measurements of R-a (**1**) exhibits two endothermic signals, which indicate crystallinity (Fig. 1). Each endothermic may belong to one of the two isomers.

Polymerization of R-a (1)

It is well known that one main drawback in benzoxazine chemistry is the high curing temperature.[3] To overcome such a disadvantage, there are promising concepts like developing new reactive benzoxazines or the application of highly active initiators. In the last decades, several effective initiators like lithium iodide,[5,25] zinc(II) triflate,[5] *p*-toluenesulfonates,[17] or phosphorus pentachloride[18] were investigated which lower the polymerization temperature dramatically. Unfortunately, these initiators also decrease the shelf-life of benzoxazine/initiator mixture. The synthesis of a potential reactive resorcinol-based benzoxazine has not been published yet. The question arises whether this structure of two electron donating aryl ether functions may be more reactive than conventional benzoxazines like the commercial bisphenol A-based one. Furthermore, it is conceivable that the application of thermolatent initiators like *p*-methoxybenzyl tetrahydrothiophenium hexafluoroantimonate (**3**) and benzyl tetrahydrothiophenium hexafluoroantimonat (**4**), which are known for effective polymerization of epoxy resins,[29,30] reduces the curing temperature of benzoxazines.

The cationic polymerization of resorcinol-based benzoxazine (**1**) was carried out (A) at 120 °C for 24 h and (B) in another approach, according to the established polymerization protocol of the commercial bisphenol A-based benzoxazine (**2**).[37] The reactivity of both the thermally induced and also the latent initiator started (in the following named super acid initiated) polymerization was investigated by DSC which is illustrated in Figure 1. The temperatures of maximum heat flow T_{peak} are listed in Table 2. R-a (**1**) has an exothermic T_{peak} value of 179 °C, which accords to the polymerization temperature and is much lower than 245 °C of BA-a (**2**). Thermolatent cationic initiators like (**3**) and (**4**), which are known for cationic polymerization of epoxy resins,[29,30] are predestinated for benzoxazine formulations with long shelf-life. The applicability of similar photoactive onium compounds has already been shown by Kasapoglu et al. for benzoxazine photopolymerization in solution.[26] The latent super acid (**3**) exhibits the lowest curing temperature with a T_{peak} of 107 °C. This drastically decreased polymerization temperature was verified by three repeated measurements. Initiator (**4**) is not as reactive as (**3**) because the *p*-methoxy group of (**3**) leads to an increased resonance stability of the formed carbocation. Further, an electron donating effect of the methoxy group activates the latent initiator which results in a lower initiation temperature as known from the polymerization of divinyl ethers.[34] All samples the pure R-a (**1**) and the mixtures with initiators (**3**) and (**4**) show a second exotherm or a shoulder, respectively. This observation may the result of multiple polymerization according to Ishida et al.[18] or probably the consequence of rearrangements which are also described in the literature.[5] The bisphenol A-

TABLE 2 DSC Peak Temperatures T_{peak} in °C for the Polymerization Reaction of the Commercial Benzoxazine (**2**) and the Resorcinol-Based Benzoxazine (**1**) With and Without Initiators (**3**) and (**4**)

	R-a (1)			BA-a (2)		
Initiator	–	(**3**)	(**4**)	–	(**3**)	(**4**)
Endothermic signal	111	73	122	41	40	42
	146	–	140	–	–	–
Exothermic signal	179	107	157	245	225	223
	229	143	–	–	–	–

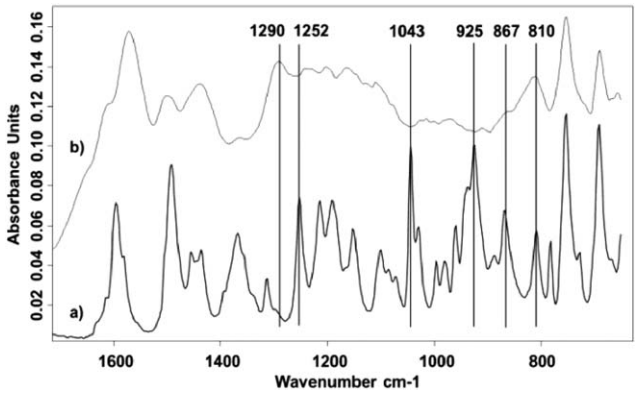
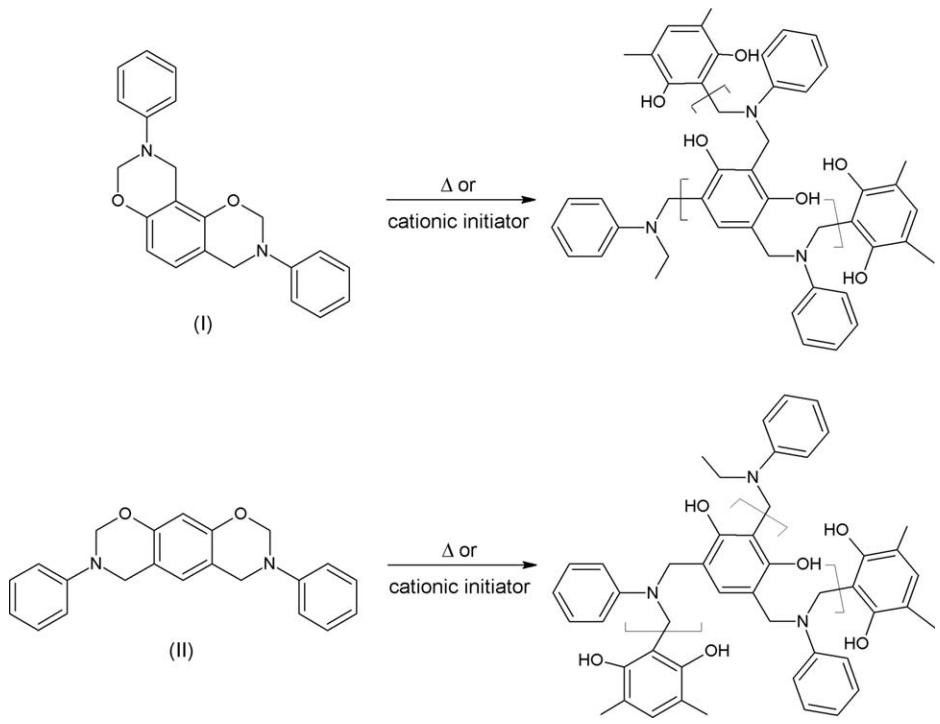


FIGURE 2 Infrared spectra of (a) R-a (**1**) and (b) poly(R-a).

based benzoxazine (**2**) exhibits only one exothermic peak for all cases shown in Table 2. The polymerization of pure BA-a (**2**) shows a T_{peak} at 245 °C but, in the presence of initiators (**3**) and (**4**), which feature identical reactivity relating to BA-a (**2**), T_{peak} is 20 °C lower. At such a high temperature, no differences in reactivity for both initiators were observed. Initiators (**3**) and (**4**) have already been both activated at significantly lower temperature compared to the polymerization temperature of the benzoxazine so that the super acid or carbocation is already available in the matrix before the polymerization temperature is reached. Although the activity of (**3**) and (**4**) is the same, it is also possible to reduce the polymerization temperature of commercial BA-a (**2**) with both latent initiators. The effect of the latent super acid (**4**) on the new resorcinol-based benzoxazine (**1**) is very similar to that of BA-a (**2**)**.** The combination of R-a (**1**) and initiator (**3**) leads to one of the lowest known polymerization temperatures for benzoxazine systems with a DSC onset temperature below 100 °C.

Infrared spectroscopy was applied for structure determination of poly(R-a). The polymerization of R-a (**1**) was performed (a) with both initiators (**3**) and (**4**) and also (b) without initiator. For both cases (a) and (b), two temperature profiles were carried out: (A) 24 h at 120 °C and (B) 2 h at 180 °C and additional 2 h at 200 °C. The reaction of R-a (**1**) without initiator and at temperature profile A) (24 h at 120 °C) is not further discussed because it is uncompleted under given conditions. The same counts for the polymerization of BA-a (**2**) with and without initiator in case of heating profile A). The IR spectra for complete conversion to poly(R-a) of both the thermally induced and the super acid initiated polymerization are identical. Poly(R-a) exhibits typical broad IR signals compared to the monomer (**1**) as can be seen in Figure 2. The aryl ether signals at 1252 and 1043 cm^{-1} disappeared after polymerization so that the presence of the phenoxy-type structure can be excluded. The polymer spectrum shows an additional signal at 1290 cm^{-1} designating the formed phenolic-type structure. Furthermore, the signals for 1,2,4,5-tetrasubstituted aromatics (isomer II) at 925 and 867 cm^{-1} disappeared after polymerization. This observation indicates a change in the degree of substitution of the aromatic ring. The broad signal at 810 cm^{-1}, which has the same value as the signal of 1,2,3,4-tetrasubstituted aromatics (isomer I), may the result of a pentasubstituted aromatic system while the presence of residual isomer (I) in the



SCHEME 2 Cationic polymerization of R-a (**1**) to pentasubstituted poly(R-a) with phenolic-type structure.

TABLE 3 Data of Thermogravimetric Analysis for Poly(R-a) and Poly(BA-a)

Samples	$T_{5\%}$ (°C)	Char Yield (%)	$\Delta m(1)$ (%)	$T_{max(1)}$ (°C)	$\Delta m(2)$ (%)	$T_{max(2)}$ (°C)
Poly(R-a)	267	56	24	292	20	416
Poly(BA-a)	327	37	42	396	22	459

polymer can be excluded because of its missing aryl ether signals. We propose the formation of a pentasubstituted phenolic-type poly(R-a) by cationic polymerization as depicted in Scheme 2. The structure of the thermally induced and super acid-initiated bisphenol A-based polybenzoxazine was also verified by IR. The infrared spectrum exhibits a phenolic-type polybenzoxazine for thermally induced polymerization corresponding to the literature.[18] As expected, the structures of the super acid-initiated and thermally induced polymerizations are the same.

TGA was carried out under nitrogen atmosphere to characterize the thermal stability of the polymers and to determine the char yield at 600 °C. The $T_{5\%}$ value is chosen as measure of thermal stability, which represents the temperature at five percent mass loss. All following TGA data are summarized in Table 3. Poly(R-a) has a $T_{5\%}$ at 267 °C which is considerably lower compared to 327 °C of poly(BA-a). That means poly(BA-a) exhibits higher thermal stability than the resorcinol based pendant. However, the thermogravimetric curves of poly(R-a) and poly(BA-a) cross each other at around 400 °C so that, henceforth, the polymeric resorcinol-based benzoxazine shows a higher thermal resistance as shown in Figure 3. Furthermore, poly(R-a) yields 56% char at 600 °C which is significantly higher compared to that one of the commercial polymerized benzoxazine with a value of 37%. Both polymers exhibit two main mass losses Δm differing in their amount and in their temperature of maximum weight loss T_{max}. Poly(R-a) has distinct lower T_{max} values but also lower amounts of mass losses which at last ends in higher char yield as described before. Hemvichian et al. demonstrated the degradation mechanism of polybenzoxazine model compounds, which decompose preferentially to amines, phenolic compounds, and benzene derivatives.[38–40] In addition, the homolytic decomposition of the hydroxyl group in phenolic compounds to form radical benzene derivatives which are able to recombine to biphenyls was described. In consideration of Hemvichians observations poly(R-a) may be able to form a diradical because of two hydroxyl groups in the resorcinol unit. This recombination of radicals may also result in higher char formation after common pyrolysis reactions. Furthermore, poly(R-a) has not got any weak iso-propyl linkage which is known for its reduction of char yield.[1] In summary poly(R-a) degrades at lower temperature but yields in significant higher char formation than poly(BA-a). It is also notable that thermal decomposition is the same independent from the usage of latent initiators (**3**) and (**4**). This observation shows that the generated super acid does not influence thermal stability negatively.

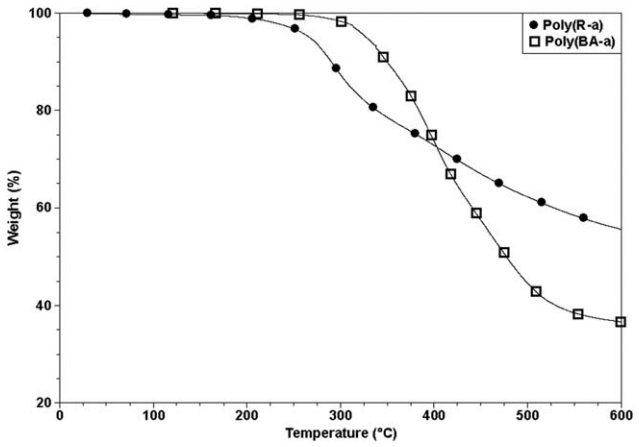


FIGURE 3 Thermogravimetric analysis of poly(R-a) and poly(BA-a) measured under nitrogen atmosphere with a heating rate of 10 K min^{-1}.

CONCLUSIONS

A new resorcinol-based benzoxazine was synthesized showing higher reactivity compared to common benzoxazines due to its specific structure. This structure offers complex electronic effects because of two meta positioned aryl ethers in the precursor and due to both the correspondent hydroxyl groups in the ring-opened form and the formed alkyl amino group in ortho- or para-position. Polymerization of benzoxazines is sensitive to electronic effects resulted from their structure as indicated for the polymerization of R-a and BA-a. The complex influence and direction of electronic effects is not yet understood completely and will be object of further examinations in which the structure of R-a will be varied systematically.

A polymerization DSC onset temperature of about 100 °C can be obtained by application with a thermolatent initiator. This is one of the lowest known curing temperatures for a benzoxazine. A complete conversion of R-a (**1**) to poly(R-a) is achieved by heating 24 h at 120 °C with a thermolatent cationic initiator. Polymerization of pure benzoxazine does not only take place at lower temperature compared to common benzoxazines but it can be also further accelerated by application of latent cationic initiators based on organic sulfonium hexafluoroantimonates. The decreased polymerization temperature of a commercial benzoxazine was not as pronounced but with 20 °C, it is significant. The drawback of high curing temperature can be overcome by the application of latent initiators preferably in combination with the resorcinol-based benzoxazine. Although the curing temperature is drastically reduced by the latent initiators, the thermal stability of formed polymers is not influenced.

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REFERENCES AND NOTES

1 H. Ishida, T. Agag, Handbook of Benzoxazine Resins; Elsevier: Amsterdam, Oxford, **2011**.

2 B. S. Rao, K. R. Reddy, S. K. Pathak, A. R. Pasala, *Polym. Int.* **2005**, *54*, 1371–1376.

3 Y. Yagci, B. Kiskan, N. N. Ghosh, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5565–5576.

4 N. N. Ghosh, B. Kiskan, Y. Yagci, *Prog. Polym. Sci.* **2007**, *32*, 1344–1391.

5 C. Liu, D. Shen, R. M. Sebastian, J. Marquet, R. Schönfeld, *Polymer* **2013**, *54*, 2873–2878.

6 F. W. Holly, A. C. Cope, *J. Am. Chem. Soc.* **1944**, *66*, 1875–1879.

7 W. J. Burke, *J. Am. Chem. Soc.* **1949**, *71*, 609–612.

8 H. J. Kim, Z. Brunovska, H. Ishida, *Polymer* **1999**, *40*, 4365–4376.

9 T. Agag, T. Takeichi, *Macromolecules* **2003**, *36*, 6010–6017.

10 T. Agag, T. Takeichi, *Macromolecules* **2001**, *34*, 7257–7263.

11 Z. Brunovska, H. Ishida, *J. Appl. Polym. Sci.* **1999**, *73*, 2937–2949.

12 H. Ishida, S. Ohba, *Polymer* **2005**, *46*, 5588–5595.

13 B. Kiskan, Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1670–1676.

14 R. Andreu, M. A. Espinosa, M. Galia, V. Cadiz, J. C. Ronda, J. A. Reina, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1529–1540.

15 B. S. Rao, A. Palanisamy, *React. Funct. Polym.* **2011**, *71*, 148–154.

16 M. Baqar, T. Agag, H. Ishida, S. Qutubuddin, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 2275–2285.

17 A. Sudo, H. Yamashita, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3631–3636.

18 Y.-X. Wang, H. Ishida, *Polymer* **1999**, *40*, 4563–4570.

19 Y.-X. Wang, H. Ishida, *Macromolecules* **2000**, *33*, 2839–2847.

20 P. Chutayothin, H. Ishida, *Macromolecules* **2010**, *43*, 4562–4572.

21 J. Dunkers, H. Ishida, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 1913–1921.

22 H. Oie, A. Mori, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4756–4761.

23 Z. Beyazkilic, M. U. Kahveci, B. Aydogan, B. Kiskan, Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4029–4036.

24 A. Sudo, S. Hirayama, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 479–484.

25 C. Liu, D. Shen, R. M. Sebastian, J. Marquet, R. Schönfeld, *Macromolecules* **2011**, *44*, 4616–4622.

26 F. Kasapoglu, I. Cianga, Y. Yagci, T. Takeichi, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3320–3328.

27 M. A. Tasdelen, B. Kiskan, Y. Yagci, *Macromol. Rapid Commun.* **2006**, *27*, 1539–1544.

28 T. Endo, H. Uno, *J. Polym. Sci. Polym. Lett. Ed.* **1985**, *23*, 359–363.

29 K. Morio, H. Murase, H. Tsuchiya, *J. Appl. Polym. Sci.* **1986**, *32*, 5727–5732.

30 A. Hartwig, K. Koschek, A. Lühring, O. Schorsch, *Polymer* **2003**, *44*, 2853–2858.

31 J. C. Crivello, In Ring-Opening Polymerization; D. J. Brunelle, Ed.; Hanser Verlag: München, **1995**; pp 157–196. Chapter 5.

32 Y. Yagci, I. Reetz, *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.

33 J. V. Crivello, K. Dietliker, Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd ed.; Wiley-VCH: Weinheim, **1998**.

34 P.-E. Sundell, S. Jönsson, A. Hult, *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1535–1543.

35 H. Oie, A. Mori, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 3867–3872.

36 A. Kikkawa, T. Takata, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1089–1095.

37 Huntsman Selector Guide, Araldite® Benzoxazine Thermoset Resins, Huntsman Corporation, **2009**.

38 K. Hemvichian, H. D. Kim, H. Ishida, *Polym. Degrad. Stab.* **2005**, *87*, 213–224.

39 K. Hemvichian, A. Laobuthee, S. Chirachanchain, H. Ishida, *Polym. Degrad. Stab.* **2002**, *76*, 1–15.

40 K. Hemvichian, H. Ishida, *Polymer* **2002**, *43*, 4391–4402.