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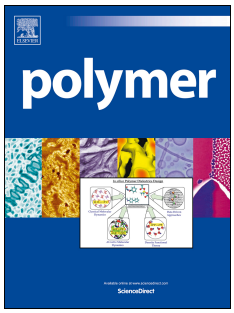

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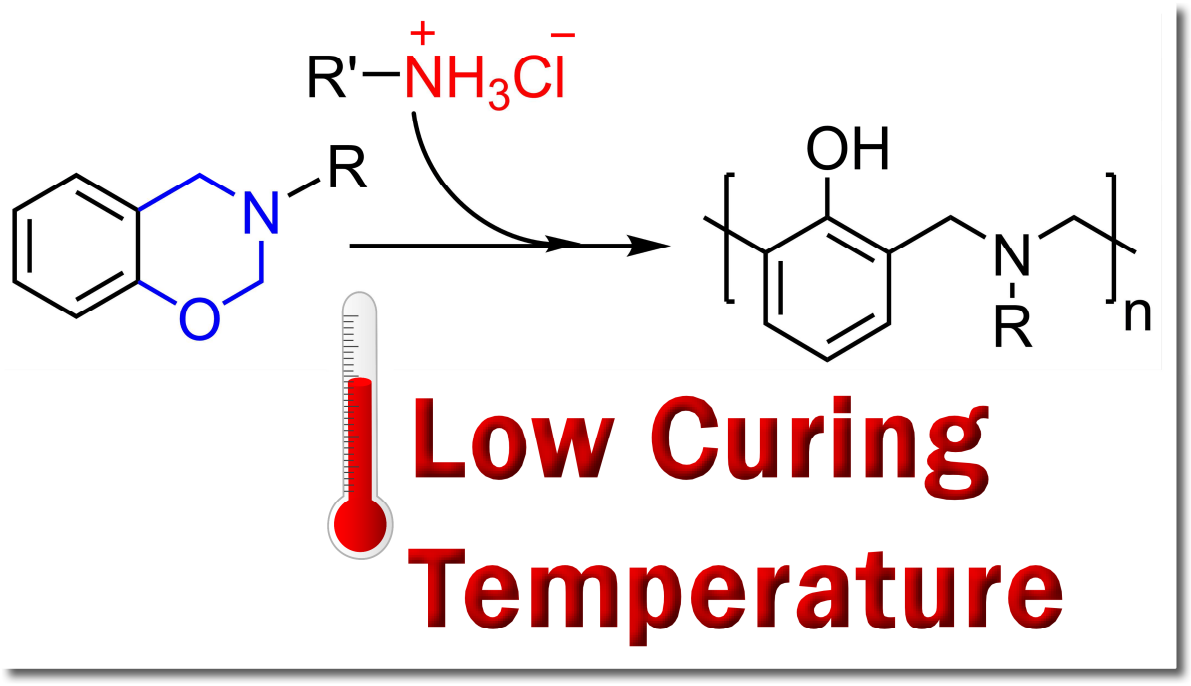

Ammonium Salt Catalyzed Ring-Opening Polymerization of 1,3-Benzoxazines

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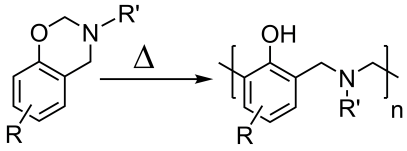
ABSTRACT

The effect of amine HCl salts as catalysts on the ring-opening polymerization (ROP) of simple 1,3-benzoxazines was investigated. The catalyst effects on the structure of the final polymer was examined and compared. The curing process for each salt-benzoxazine mixture was monitored by using Differential Scanning Calorimetry (DSC) and it was found that amine salts cause clear reduction in ROP temperature. As followed by ^{1}H NMR investigations, the ring-opening of oxazine can take place even at r.t. when suitable solvent is used. Moreover, the analysis gave evidences that amine HCl salts act as nucleophilic catalyst and their efficiency is dependent on ionization ability and solubility of the salts. Thermal stability of the final polymers was also analyzed using Thermal Gravimetric Analysis (TGA).

Keywords: Benzoxazine, Amine Salt, Ring-opening polymerization, Curing, Polybenzoxazine,

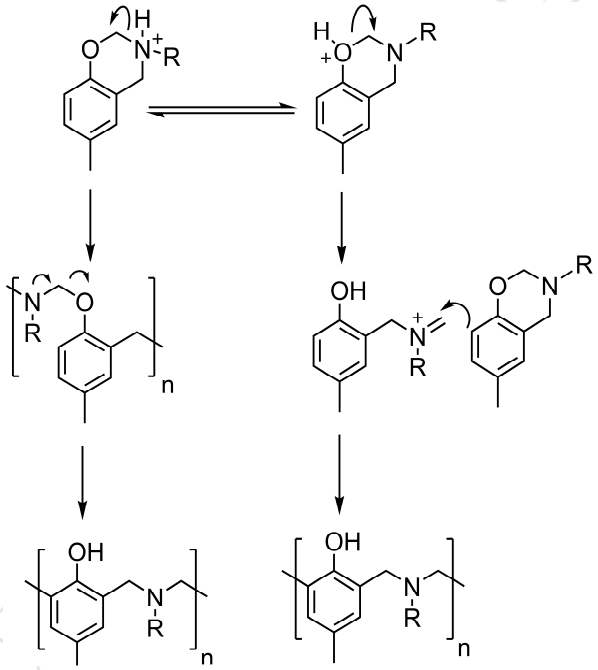
INTRODUCTION

Polybenzoxazines (PBZs) as alternative contender to classical phenolics have emerged in the last few decades and become one of the rare polymers found industrial applications. This is mainly due to their unique structural features such as high glass transition temperatures (T_g) (170–340 °C), char yields (generally 20–60% at 800 °C), tensile strength and modulus (100–125 MPa, 3.8–4.5 GPa, respectively), flame retardancy with low smoke and toxicity, limited water uptake, dimensional stability during curing and resistance against acids and bases.[1-4] Consequently, these materials have high service temperatures and their stability under harsh conditions makes them good candidates especially for aerospace and similar applications.[5] The structural difference between PBZs and other phenolic resins is the presence of tertiary amine group in each repeat unit, which generate a great number of intra- and inter-molecular hydrogen bonds that determine many properties of these materials.[6-11] PBZs are obtained from their corresponding 1,3-benzoxazine monomers via ring-opening polymerization (ROP) of oxazine moiety (Scheme 1). The polymerization is thermally driven and temperatures between 140–220 °C, sometimes even more, are required for the ring-opening process depending on the monomer structure.[12-14] Although, low ROP temperatures are often observed for specially designed monomers such as carboxylic acid or phenolic –OH containing benzoxazines,[15-20] common benzoxazine monomers have ROP temperatures over 220 °C when dynamic heating is applied.[21-23]



Scheme 1: Ring-opening polymerization of 1,3-benzoxazine monomer yielding PBZ.

It is generally accepted that the polymerization proceeds over a kind of cationic pathway initiated by the reaction of residual phenolic –OH of monomers and oxazine ring. This issue was simply tested by using pure benzoxazines and ROP temperatures increased drastically. The N and O atoms present on the oxazine ring stabilize the cations formed and ring-opening takes place with a subsequent electrophilic aromatic substitution to form PBZ. As expected, there is two protonation possibility either on N or O atom and thus, initiation of polymerization proceeds concomitantly in two routes. [24-28] Although, the initiation site has effect on the intermediates, the final polymer for both pathways is considered to have the same structure (Scheme 2).



Scheme 2: Proposed polymerization mechanisms for 1,3-benzoxazines initiated by protonation of either N or O atoms. [24-28]

Though the ROP of benzoxazines does not require additional catalyst or curative, high curing temperature is an obvious restriction both in terms of energy consumption and limitation on the usage of thermally susceptible functional groups on PBZs. Hence, lower ROP temperatures would be a significant advantage. To address this issue, several catalysts such as organic or Lewis

acids and compounds bearing nucleophilic character have been employed to promote the ROP. For example, PCl_5, $POCl_3$, $TiCl_4$, $AlCl_3$, $FeCl_3$ with solvents have been shown to have good catalytic activities.[25, 28-30] Another important example concerns the use of the mixture of a Lewis acid and a nucleophilic catalyst to effectively promote the polymerization. Typically, acetylacetonato complexes of transition metals of the 4th period was found to act as highly efficient catalysts.[31] However, the admixing of such active catalysts to benzoxazines often initiates ROP at r.t. and increases the viscosity significantly during the storage, thus, reducing the shelf life in practical use. Latent catalysts, dormant at r.t. or certain temperatures, but generate active initiators by heating were shown to overcome such storage problems. For example, toluene sulfonates, diamines, thiols and elemental sulfur were successfully used to reduce ROP temperatures for classical mono- and di-functional benzoxazines.[32-41] Apart from admixed catalysts, specially designed benzoxazine monomers can also be used as latent catalysts. Generally, free phenolic –OH group bearing benzoxazines or naphthoxazines are able to reduce the ROP temperature to certain values.[19, 42] Despite these considerable efforts, a further reduction of polymerization temperature with cheap catalysts is highly desirable and major concern for benzoxazine based high performance thermosets. Herein, we are interested in developing a latent catalyst based on amine HCl salts to reduce the ROP of benzoxazines to practical temperatures.

EXPERIMENTAL

Materials

Paraformaldehyde (Aldrich, 96%), aniline (Merck, 99.5%), 4,4′- isopropylidenediphenol (Alfa Aesar, 97%), 1,4-dioxane (Merck, 99%), diethyl ether (Merck, 99.7%), sodium hydroxide (Merck, 99%), aAmmonium chloride (Merck, 99.8%), phenylhydrazine hydrochloride (Fluka

AG, 99%), anilinium hydrochloride (Merck, 97%), benzyl triethyl ammonium chloride, hydroxy ammonium chloride (Merck, 99%), ethylamine hydrochloride (Sigma-Aldrich, 98%)

Characterization

All ^{1}H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ or DMSO-d_6 with $Si(CH_3)_4$ as an internal standard. FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer. Differential Scanning Calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC from 30 °C to 320 °C with a heating rate of 10 °C.min^{-1}. under nitrogen flow. A typical DSC sample was 2–5 mg in a 30 μL aluminum pan. Thermal gravimetric analysis (TGA) was performed on Perkin-Elmer Diamond TA/TGA with a heating rate of 10 °C.min^{-1}. under nitrogen flow.

Synthesis of Monomers

Bisbenzoxazine monomer (BA-a) synthesis was performed according to the literature [43]. In a 250 mL round bottomed flask, 3 g (100 mmol) of paraformaldehyde, 2.33 g (25 mmol) aniline, 5.7 g (25 mmol) bisphenol A and were dissolved in 180 mL 1,4-dioxane and the reaction mixture was refluxed for 12h. After completing reaction, 1,4-dioxane was completely evaporated using a rotary evaporator. The remaining sticky crude product was dissolved in 150 mL diethylether and washed with 200 mL, 0.2 M NaOH solution in three portions, then, washed with 100 mL distilled water. After washing process, the solution was dried using anhydrous Na_2SO_4. After filtering the drying agent, diethyl ether was removed under reduced pressure. The remaining semi-solid was dried under vacuum at 50 °C for 24h, resulted a solid (yield≈ 52 %). Note: In the case of mono-functional monomers phenol, paraformaldehyde, *p*-Toluidine and benzylamine were used. Mono-

functional monomers are abbreviated as P-tol (*p*-Toluidine derived) and P-bz (benzyl amine derived).

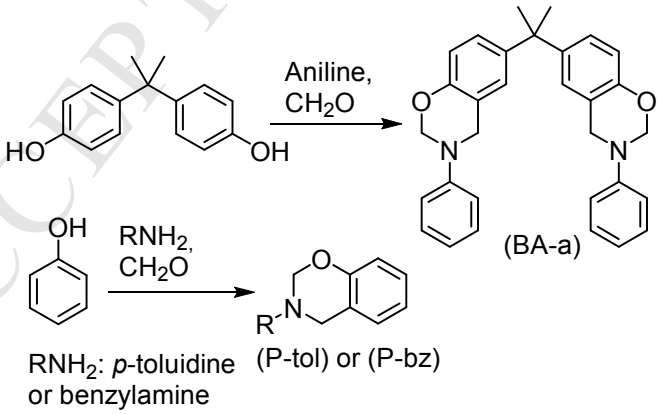
Curing Procedure

Typical curing procedure is as follows: BA-a or P-tol monomer was mixed with a selected amine HCl salt (5 mol%) by grinding in a mortar with a pestle. Acetone (2-3 mL) was added to this mixture and all the mass was stirred with a spatula for 1-2 min. Then, acetone was removed by blowing air or N_2 gas. The remaining mixture placed in a Teflon mold and then heated up to 170-220 °C according to the DSC data for each admixed amine HCl salt.

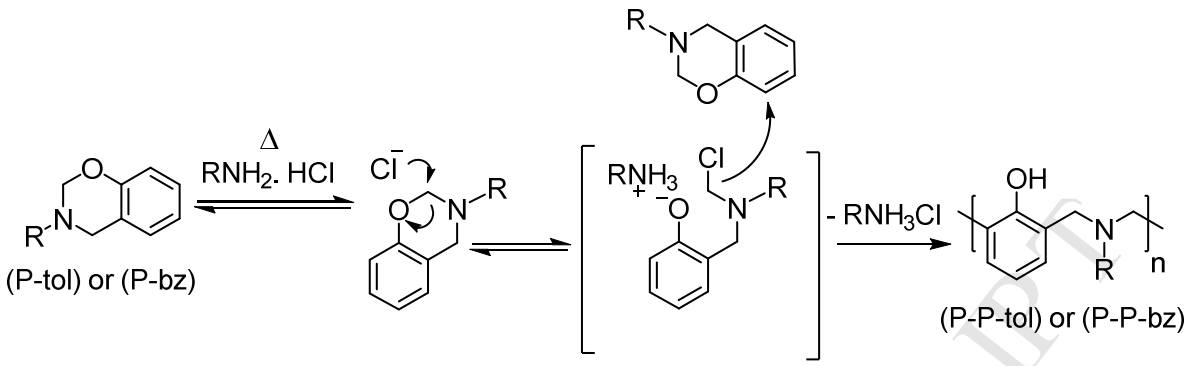
RESULTS AND DISCUSSIONS

As stated, previous studies on the polymerization mechanism of benzoxazines disclosed that ROP begins by the cleavage of methylene bridge on the oxazine ring. Formation of different cationic intermediates by thermal activation followed by N-, O- and aryl attack and rearrangement of labile bonds finally produce polybenzoxazines. In a such mechanism, latent activation of catalyst during benzoxazine curing would be beneficial both to lower the ROP temperature and solve the storage problems. Addition to this classical pathway, initiation by a nucleophile by using primary amines was shown to be an alternative route.[32, 35] It was revealed that nucleophilic catalysts have the capacity to reduce ROP temperature and could act as latent catalyst in certain formulations. In the light of these developments, it seemed appropriate to consider amine HCl salts as a latent catalyst system since most of the amine HCl salts are very stable compounds at r.t. and do not release HCl or any other species. However, at certain temperatures an equilibrium may be established between amine and its HCl salt form. For example, ammonium chloride decomposes into ammonia and hydrogen chloride gas upon heating.[44] And after such

decomposition, the released HCl would eventually act as initiator for ROP of benzoxazines by protonation of N and O atom. However, this possibility is so small since decomposition of many amine HCl salts have higher temperatures than required for ROP of benzoxazines. Apart from this excluded pathway, amine HCl salts can ionize at certain temperatures in melt benzoxazine and generate chlorine anion that could act as nucleophilic catalyst. It should be noted that the ionization of many salts is limited in organic compounds and thus, in a benzoxazine medium, solubility and ionization constant of the salt, polarity of benzoxazine monomer would affect the catalyst performance. In order to gain more insight on the influence of amine HCl salts on ROP of benzoxazines, first, classical benzoxazine monomers derived from bisphenol A and phenol was synthesized using aniline, *p*-toluidine and benzylamine as amine sources by the conventional method (Scheme 3). Their thermally activated curing behavior in the presence and absence of several amine salts was investigated and plausible mechanism for the ring-opening process was proposed (Scheme 4).



Scheme 3: Synthesis of benzoxazine monomers.



Scheme 4: Plausible mechanism for ROP of 1,3-benzoxazines with ammonium salts.

Spectral characterization of these monomers was performed using ^{1}H NMR and FTIR spectroscopies (Figure S1, S2, S3).

As stated, depending on the functionalities present, benzoxazines have the ROP temperature (Curing maximum, T_{max}) generally over 220 °C and this event can be monitored as an exotherm. Thus, ROP of BA-a, P-tol and P-bz with amine salts were analyzed under N_2 environment with a heating rate of 10 °C. min^{-1} using a DSC device. Accordingly, samples were prepared as follows: P-tol and BA-a monomers were mixed with several amine salts by grinding with a mortar and pestle. Acetone was also added to these mixtures to obtain a better homogeneity, and immediately evaporated by using air or N_2 blow. The overlaid DSC thermograms for P-tol and its amine salt mixtures presented in Figure 1 and tabulated DSC data in Table 1 disclose the ROP reduction trend according to the used amine HCl salt. The results clearly indicate that amine HCl salts have a positive effect on the ROP temperature of P-tol monomer. The most ROP temperature depression is provided by hydroxylamine HCl salt. Besides, aromatic amine salts are also highly effective on ROP temperature. The impact of catalyst amount on ROP was also analyzed by increasing the anilinium chloride content from 5 to 10 mol% and the on-set of curing temperature dropped to 158 °C. Actually, similar effect was observed for each salt, but we

deliberately kept the catalyst amount as 5 mol% because high amounts of the salt content in polybenzoxazines may generate voids and phase separation that eventually affect the physical properties in a deleterious manner.

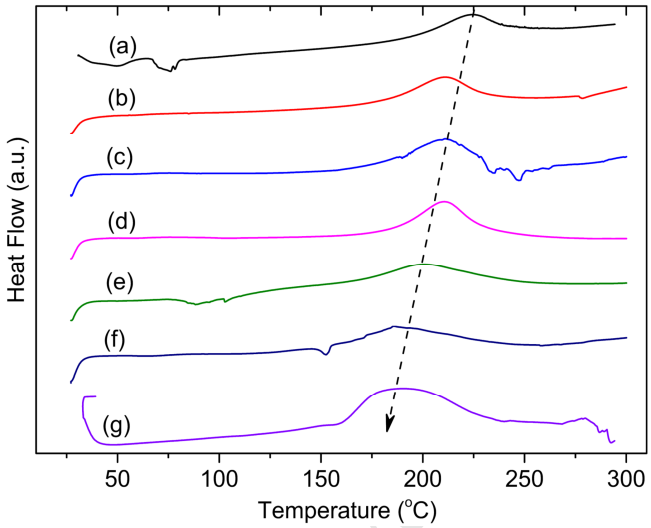


Figure 1: DSC Thermograms of P-tol and amine HCl salt mixtures (5 mol%), P-tol (a), P-tol/$EtNH_3Cl$ (b), P-tol/NH_4Cl (c), P-tol/$PhNH_3Cl$ (d), P-tol/$PhNHNH_3Cl$ (e), P-tol/NH_3OHCl (f), P-tol/$PhNH_3Cl$ (10 mol%)

Table 1: DSC Thermogram data of P-tol/amine salts (5 mol%) mixtures

Sample	On-Set of Curing (°C)	End-Set of Curing (°C)	Maximum Curing Temp. (C^o)	Amount of Exotherm (J/g)
P-tol	190	237	224	-124
P-tol/NH_3OHCl	167	232	185	-156
P-tol/$PhNH_3Cl$	173	225	205	-74
P-tol/$PhNH_3Cl$ (10 mol %)	158	236	189	-161
P-tol/$PhNHNH_3Cl$	166	240	200	-110
P-tol/NH_4Cl	189	222	210	-84

P-tol/EtNH$_3$Cl	181	232	210	-160

Similar trend was observed for the BA-a monomer and salt mixtures (Figure 2 and Table 2). Aromatic amine salts are the most effective salts in this case and $NH_2OH.HCl$ has a drastic ROP temperature lowering effect, too. For both monomers, aromatic amine HCl salts are effective that signifying the importance of solubility of the salts in melt benzoxazine.

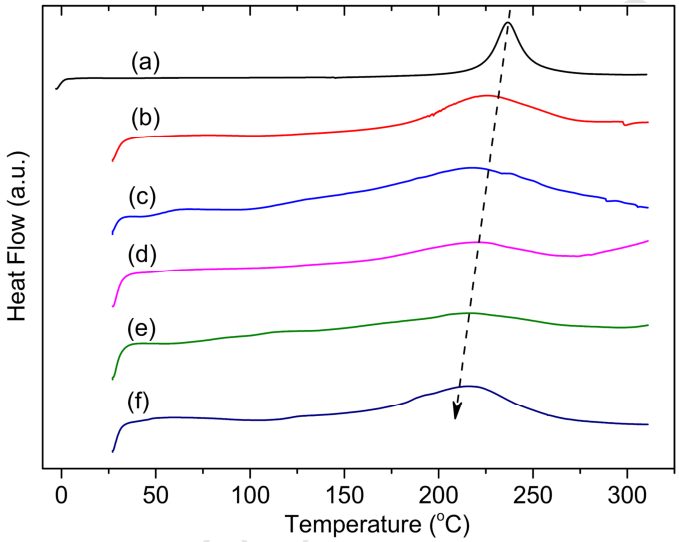


Figure 2: DSC Thermograms of BA-a and amine HCl salt mixtures (5 mol %), BA-a (a), BA-a/ NH_4Cl (b), BA-a/$EtNH_3Cl$ (c), BA-a/NH_3OHCl (d), BA-a/$PhNHNH_3Cl$ (e), BA-a/$PhNH_3Cl$ (f)

Table 2: DSC Thermogram data of BA-a/amine salts (5 mol %) mixtures

Sample	On-Set of Curing (°C)	End-Set of Curing (°C)	Maximum Curing Temp. (°C)	Amount of Exotherm (J/g)
BA-a	211	260	237	-125
BA-a/NH$_3$OHCl	170	255	214	-106
BA-a/PhNH$_3$Cl	174	242	213	-35
BA-a/PhNHNH$_3$Cl	170	255	213	-105

BA-a/NH_4Cl	181	254	208	-124
BA-a/$EtNH_3Cl$	171	255	216	-108

In contrast, the solubility of NH_3OHCl can be expected to be relatively lower compared to aromatic amine HCl and $EtNH_3Cl$ in benzoxazines. However, this salt is more effective than NH_4Cl, $EtNH_3Cl$ for both monomers and as effective as aromatic amine salts. To further clarify this issue, DSC analysis was performed to check whether a decomposition takes place or any exotherm overlaps is present during curing for NH_3OHCl catalyst. In Figure 3, DSC traces of P-bz, NH_3OHCl and P-bz/NH_3OHCl (2:1, w/w) are presented. Notably, high amount of catalyst is used to augment any effect for clarity. As seen, this salt has a melting at 158 °C and a rigorous exotherm after T_m, probably due to decomposition, and an evaporation endotherm starting at 220 °C. Thus, the catalyzing mechanism for this salt can be different than proposed for the other amine HCl salts. Moreover, when this salt is mixed with P-bz the on-set of ROP temperature decreases drastically down to 91 °C and T_{max} lowered from 260 to 155 °C. However, this pronounced effect was observed in the case of high amount of NH_3OHCl in benzoxazine.

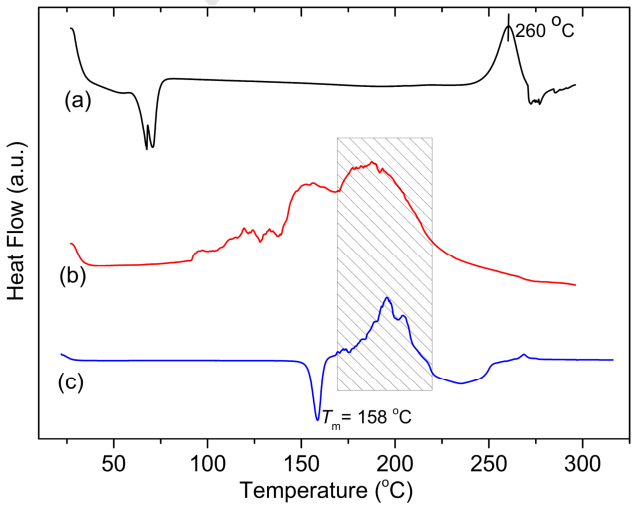


Figure 3: DSC thermograms of P-bz (a), P-bz/NH_3OHCl (2:1, w/w) (b), NH_3OHCl (c)

As stated, the solubility of amine HCl salts in the reaction medium is crucial factor for ring-opening of benzoxazines. Hence, it can be expected that in suitable solvents, amine HCl salts can catalyze the ROP more easily. It is even likely that ring-opening can be achieved at r.t. in certain solvents. However, it is important to point out that it does not mean that the polymerization can take place at r.t. To test this probability, we have conducted a reaction followed by ^{1}H NMR spectroscopy. P-tol and anilinium chloride was dissolved in $CDCl_3$ and NMR spectrum was recorded immediately. Then, after 1h, 3h, 6h and 24h ^{1}H NMR spectra of the same sample were taken to track N-CH_2-O protons of oxazine ring (Figure 4). It is obvious that in solution medium the catalytic effect of amine HCl salt is operative and ring-opening takes places at r.t. These results can also be considered as an evidence for the role of Cl^- ions on the mechanism. Since amine HCl salts cannot decompose at r.t. to form HCl, the possible formation and catalyzing effect of HCl can be excluded from the ROP mechanism.

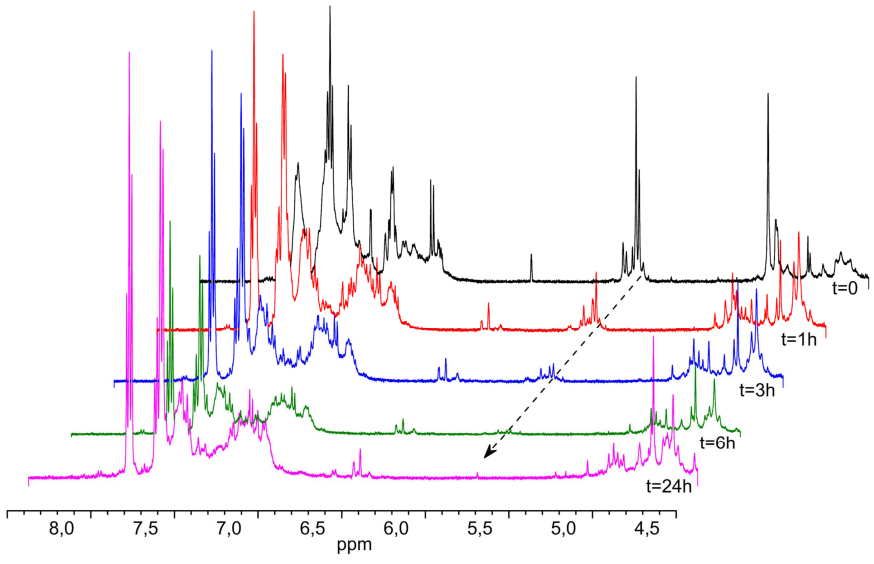


Figure 4: ^{1}H NMR spectra of BA-a/$PhNH_3Cl$ mixture in $CDCl_3$ at r.t. for given interaction period.

The effect of the catalyst on the structure of the final polymer was also investigated by FTIR analysis. The overlaid FTIR spectra of the resulting polymers after catalytic and non-catalytic curing of P-tol are presented in Figure S4. Only minor or no change in the spectra is noted indicating that varying the amine HCl salts have limited or no impact on the end-structure.

Thermal stability of the polybenzoxazines for each catalyst was measured by using thermo-gravimetric analysis (TGA). TGA traces and related thermal properties are presented in Figure 5 and Table 3, respectively. According to TGA data, amine salt catalyzed polybenzoxazines have slight difference for $T_{5\%}$, $T_{10\%}$ and T_c. In terms of initial degradations, except NH_4Cl catalyzed sample, the other samples have slight lower values and among them $PhNHNH_3Cl$ catalyzed sample has the lowest value. However, the same sample has a char yield value as that of the cured P-tol (P-P-tol). The degradation patterns of the samples, except aromatic salt catalyzed, exhibit similarities according to T_{max} values with three maxima. These analogous patterns can also be seen in derivative TGA graph in Figure S5. Moreover, char yields at 800 °C are close and lies between 20–28%. But, it should be noted that all the samples have lower char yields than pristine P-P-tol. There are two possible explanations for the observed char yield depression. One is that amine salts lead to lower char formation effecting the degradation pathways of polybenzoxazines, and the other is the decomposition and evaporation of the amine salt at the elevated temperature since those molecules are not part of the polybenzoxazine networks. When the char yields are compared, the mass difference is close to the added amount of salt for most samples which may be considered as a support for the second possibility. On the contrary, T_{max} values of the catalyzed samples are better than values for P-P-tol, possibly amine salts generate a stiffer network.

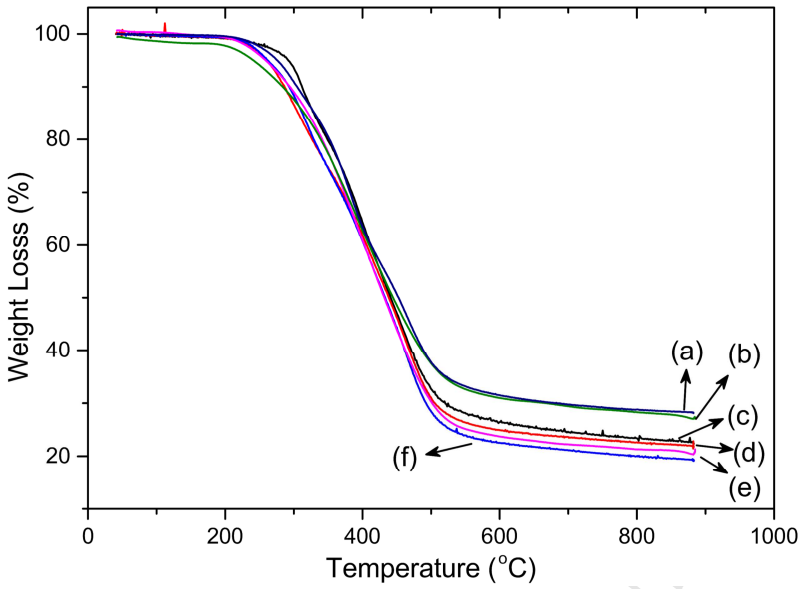


Figure 5: TGA traces of cured P-tol and amine salts (5 mol%) mixtures, P-tol (a), P-tol/$PhNHNH_3Cl$ (b), P-tol/NH_4Cl (c), P-tol/NH_3OHCl (d), P-tol/$PhNH_3Cl$ (e), P-tol/$EtNH_3Cl$ (f)

Table 3: Thermal properties of the cured P-tol and amine salts (5 mol%) mixtures

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)[a]	T_c (%)
P-tol	275	305	296, 378, 466	28
P-tol/$PhNHNH_3Cl$	242	284	390	28
P-tol/NH_4Cl	292	311	314, 399, 458	23
P-tol/NH_3OHCl	261	285	300, 404, 460	22
P-tol/$PhNH_3Cl$	258	294	393	21
P-tol/$EtNH_3Cl$	261	291	316, 407, 460	20

[a] These values extracted from derivative of TGA (Fig. S5 in supporting information).
$T_{5\%}$: The temperature for which the weight loss is 5%
$T_{10\%}$: The temperature for which the weight loss is 10%
T_{max}: The temperature for maximum weight loss.
T_c: The char yield at 800 °C

CONCLUSION

We have established the catalytic potential of various amine HCl salts in the polymerization of benzoxazines. The results revealed that solubility and ionization of the salts in melt benzoxazine

play important roles in the catalytic ability. The stability of the salts and ^{1}H NMR analysis give evidences that the nucleophilic initiation is operative in which amine HCl salts catalyze the ROP via Cl^- attack on the oxazine ring. However, after initial stages of ring-opening, the formed free phenolics can alter the pathway and cationic species predominate the mechanism. Thus, both the anionic and cationic species may involve in the overall polymerization process. It should also be noted that among the amine HCl salts, NH_3OHCl appears to have different thermal behavior and exhibits an exotherm after its melting point overlapping ROP exotherm of benzoxazines. Moreover, FTIR analysis were conducted to detect possible differences in the end-structures and it was found that there is no or limited catalytic impact on the PBZ. It is clear that amine HCl salts can be used as an effective and cheap catalyst for ROP of benzoxazines. The ability of the salts to reduce the maximum ROP temperatures, *e.g.* down to 184 from 224 °C, may lead to further extend industrial applications these high performance thermosets.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Additional Information

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests

The authors declare no competing financial interests.

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Highlights

- Ammonium salts reduced the ring-opening polymerization temperature of 1,3-benzoxazines.
- Availability and cost of ammonium salts are additional advantages.