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# Novel Chiral and Achiral Benzoxazine Monomers and Their Thermal Polymerization

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ABSTRACT: New chiral and achiral benzoxazine monomers (*S*)-α-3-methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine and *rac*-α-3-methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine were prepared by Mannich condensation from enantiomerically pure (*S*-α) and racemic (*rac*) methylbenzylamine $H_2NCH(CH_3)C_6H_5$, formaldehyde and 2,4-di-*tert*-butylphenol. Their DSC exhibit exotherms at 291 and 263 °C which correspond to oxazine thermal polymerization. The resulted polymers show very low $T_g$ values of 31 and 19 °C for poly-*S*-**1** and poly-*rac*-**1**, respectively. Higher value for the polymer obtained from enantiomerically pure monomer results from the monomer derived stereoregularity of the polymer. A comparison of thermal stabilities of both polymers showed significantly lower heat resistance for the polymer obtained from racemic monomer. The resulted data are compared with those obtained for similar *rac*-α-3-methylbenzyl-3,4-dihydro-8-(1,1,3,3-*tetra*-methylbutyl)-2*H*-1,3-benzoxazine with a free *ortho* position at the phenyl.

## Introduction

Benzoxazines are biheterocycles generated for instance by the Mannich-like condensation of a phenol, formaldehyde and an amine.[1] As it was very well evidenced, they constitute excellent precursors to a large family of phenolic resins.[2] They have also been well recognized for their broad range of biological activity.[3] Thermal polymerization of substituted 3,4-dihydro-2*H*-1,3-benzoxazines generates polybenzoxazines which offer excellent mechanical, physical and thermal properties.[2,4] The major disadvantages of polybenzoxazines are their brittleness and a high temperature needed for the ring-opening polymerization. From these reasons, their further performance enhancement is highly expected. In this regard, a preparation of copolymers,[5] polymer alloys,[6] composites, and blends[7] becomes increasingly attractive. Another effective approach to enhance their performance is a preparation of novel polybenzoxazines from monomers containing functional or polymerizable group.[8] These approaches successfully afforded polymers with high glass transition temperature and improved decomposition temperature in comparison to typical polybenzoxazines.[2]

Although more and more interesting research results on polymerization of different benzoxazines are lately being published we have been surprised by the lack of literature concerning the polymerization of chiral monomeric precursors. We envision this as a notable point which, as we believe, should conscientously be investigated. With this in mind, we prepared and characterized a novel benzoxazine monomer modified by the chiral substituent (*S*)-α-methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine. The compound was characterized by X-ray diffraction and its thermal polymerization has been described. In order to reveal the influence of chirality on the polymerization process and resulted polymer properties (*rac*)-α-methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine has also been obtained and polymerized. Finally, polymerization of both precursors has been compared with the same process of (*rac*)-3-methylbenzyl-3, 4-dihydro-8-(1,1,3,3-*tetra*-methylbutyl)- 2*H*-1,3-benzoxazine, a monomer with a free *ortho* position.

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## Experimental Data

Solvents were treated as follows: MeOH, distilled from Mg. 2,4-di-*tert*-butylphenol, (*S*)-α-methylbenzylamine, *rac*-methylbenzylamine and formaldehyde (37% aqueous solution) were purchased from Aldrich and used as received. $CDCl_3$ (Cambridge Isotope Laboratories) was distilled from $CaH_2$. $^1H$ and $^{13}C$ NMR spectra were detected using Bruker ESP 300E or 500 MHz spectrometer. Chemical shift data are reported in parts per million and referenced to the residual protons in $CDCl_3$. Differential scanning calorimetry was conducted using a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min under dinitrogen. Thermogravimetric analysis (TGA) was determinated with a SETARAM Setsys TG-DTA 16 at a heating rate of 2 °C/min under $N_2$. The samples for IR analysis were mixed with dried KBr powder, pressed into a pellet for recording IR spectra with a IFS 66/S (Bruker, Germany). Mass spectrometric measurements were performed using a micrOTOF-Q (Bruker, Germany) electrospray mass spectrometer. Specific rotation was measured using a Jasco DIP-1000 Digital Polarimeter.

**(*S*)-α-3-Methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl- 2*H*-1, 3-benzoxazine (*S*-1).** A solution of 2,4-di-*tert*-$BuC_6H_3OH$ (4.87 g, 23.6 mmol), (*S*)-α-methylbenzylamine (2.86 g, 23.6 mmol) and formaldehyde (4.41 mL, 37% aqueous solution, 2.5 equiv) in methanol (30 mL) was stirred and refluxed for 36 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The remaining yellowish oil was dissolved in cold methanol (10 mL) and cooled down in a freezer to give pale yellow crystals of *S*-**1** (6.72 g, 19.2 mmol, 81%). Calcd for $C_{24}H_{33}NO$ (351.53): C, 82.00; H, 9.46; N, 3.98. Found: C, 81.90; H, 9.41; N, 3.92. mp = 78.8 °C. $[\alpha]_{589} = -41.3°$ (0.59, EtOH). For poly-*S*-**1** $[\alpha]_{589} = 8.21°$ (0.30, EtOH). MS (ESI): 351 (100%) $[M^+]$.

FT-IR (KBr): 535 m, 560 m, 601 w, 646 w, 696 vs, 745 m, 775 vs, 784 m, 819 w, 837 vw, 888 w, 905 s, 947 vs, 1001 m, 1019 w, 1093 m, 1118 s, 1136 s, 1155 m, 1205 s, 1223 vs, 1263 w, 1299 m,

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1340 w, 1358 s, 1384 s, 1414 w, 1453 vs, 1476 vs, 1602 w, 2901 s, 2954 vs.

$^1$H NMR ($CDCl_3$, 297 K): $\delta$ = 1.27, 1.39 (2s, 18H, C($CH_3$)$_3$), 1.46 (d, $J_{HH}$ = 6.7 Hz, 3H, $CH_3$), 3.97 (q, $J_{HH}$ = 6.7 Hz, 1H, CH), 3.85, 4.14 (2d, $J_{HH}$ = 16.4 Hz, 2H, N−$CH_2$−Ar), 4.77, 5.03 (2d, $J_{HH}$ = 10.5 Hz, 2H, O−$CH_2$−N), 6.73, 7.16 (2d, $J_{HH}$ = 1.9 Hz, 2H, Ar), 7.24−7.40 (m, 5H, Ph).

$^{13}$C NMR ($CDCl_3$, 297 K): $\delta$ = 21.5 (1C, NCHPh$CH_3$), 29.6 (3C, C($CH_3$)$_3$), 31.6 (3C, C($CH_3$)$_3$), 34.2, (1C, C($CH_3$)$_3$), 34.7 (1C, C($CH_3$)$_3$), 49.4 (1C, N-$CH_2$−Ar), 57.6 (NCHPh$CH_3$), 79.4 (1C, O-$CH_2$−N), 122.0 (1C, *o*-C(Ar)−$CH_2$−N), 123.5, 124.1 (2C, *m*-C(Ar)), 127.1 (1C, *p*-C(Ph)), 127.4 (2C, *m*-C(Ph)), 128.4 (2C, *o*-C(Ph)), 136.2 (1C, *o*-C(Ar)C($CH_3$)$_3$), 141.9 (1C, *p*-C(Ar)C($CH_3$)$_3$), 144.8 (1C, *i*-C(Ph)−CH), 151.1 (1C, *i*-C(Ar)−O).

**(*S*)-α-3-Methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine 2,4-Di-*tert*-Bu$C_6H_3$OH Solvate (*S*-1·2,4-di-*tert*-Bu$C_6H_3$OH).** *S*-**1** (0.52 g, 1.48 mmol) was dissolved in methanol (20 mL) and 1 equiv of 2,4-di-*tert*-Bu$C_6H_3$OH (0.31 g, 1.48 mmol) was added. The solution was stirred for 15 min and the volume was reduced to ca. 5 mL and placed in a fridge to give overnight crystalline *S*-**1**·2,4-di-*tert*-Bu$C_6H_3$OH in 93% yield (0.77 g, 1.38 mmol). Anal. Calcd for $C_{38}H_{55}NO_2$ (557.83): C, 81.82; H, 9.94; N, 2.51. Found: C, 81.91; H, 9.91; N, 2.54.

***rac*-α-3-Methylbenzyl-3,4-dihydro-6,8-di-*tert*-butyl-2*H*-1,3-benzoxazine (*rac*-1).** 2,4-Di-*tert*-Bu$C_6H_3$OH (8.09 g, 39.3 mmol), *rac*-methylbenzylamine (4.76 g, 39.3 mmol) and formaldehyde (7.35 mL, 37% aqueous solution, 2.5 equiv) and methanol (50 mL) were combined in a procedure analogous to that for *S*-**1**. Analogous workup gave *rac*-**1** as pale yellow crystals in 85% yield (11.74 g, 33.4 mmol). Calcd for $C_{24}H_{33}NO$ (351.53): C, 82.00; H, 9.46; N, 3.98. Found: C, 81.97; H, 9.43; N, 3.90. mp = 111.8 °C.

FT-IR (KBr): 532 w, 564 w, 601 w, 649 w, 697 vs, 751 s, 773 m, 788 w, 817 vw, 837 vw, 881 m, 906 m, 951 vs, 1000 m, 1016 w, 1086 w, 1119 m, 1140 s, 1155 m, 1201 m, 1224 vs, 1279 w, 1301 w, 1340 w, 1359 m, 1385 m, 1414 w, 1453 s, 1476 vs, 1601 w, 2901 s, 2959 vs.

$^1$H NMR ($CDCl_3$, 297 K): $\delta$ = 1.27, 1.39 (2s, 18H, C($CH_3$)$_3$), 1.46 (d, $J_{HH}$ = 6.7 Hz, 3H, $CH_3$), 3.97 (q, $J_{HH}$ = 6.7 Hz, 1H, CH), 3.85, 4.14 (2d, $J_{HH}$ = 16.4 Hz, 2H, N−$CH_2$−Ar), 4.77, 5.03 (2d, $J_{HH}$ = 10.5 Hz, 2H, O−$CH_2$-N), 6.73, 7.16 (2d, $J_{HH}$ = 1.9 Hz, 2H, Ar), 7.24−7.40 (m, 5H, Ph).

$^{13}$C NMR ($CDCl_3$, 297 K): $\delta$ = 21.5 (1C, NCHPh$CH_3$), 29.6 (3C, C($CH_3$)$_3$), 31.6 (3C, C($CH_3$)$_3$), 34.2 (1C, C($CH_3$)$_3$), 34.7 (1C, C($CH_3$)$_3$), 49.4 (1C, N−$CH_2$−Ar), 57.6 (NCHPh$CH_3$), 79.4 (1C, O−$CH_2$−N), 122.0 (1C, *o*-C(Ar)−$CH_2$−N), 123.5, 124.1 (2C, *m*-C(Ar)), 127.1 (1C, *p*-C(Ph)), 127.4 (2C, *m*-C(Ph)), 128.4 (2C, *o*-C(Ph)), 136.2 (1C, *o*-C(Ar)C($CH_3$)$_3$), 141.9 (1C, *p*-C(Ar)C($CH_3$)$_3$), 144.8 (1C, *i*-C(Ph)−CH), 151.1 (1C, *i*-C(Ar)−O).

***rac*-α-3-Methylbenzyl-3,4-dihydro-8-(1,1,3,3-tetramethylbutyl)-2*H*-1,3-benzoxazine (*rac*-2).** 4-(1,1,3,3-Tetramethylbutyl)-phenol (1.00 g, 4.85 mmol), *rac*-methylbenzylamine (0.59 g, 4.85 mmol), formaldehyde (0.91 mL, 37% aqueous solution, 2.5 equiv) and methanol (10 mL) were combined in a procedure analogous to that for *S*-**1**. Analogous workup gave *rac*-**2** as colorless crystals in 82% yield (1.40 g, 3.98 mmol). Anal. Calcd for $C_{24}H_{33}NO$ (351.53): C, 82.00; H, 9.46; N, 3.98. Found: C, 81.95; H, 9.45; N, 3.92. Mp = 62.6 °C.

FT-IR (KBr): 440 w, 481 w, 537 w, 578 w, 622 w, 660 w, 697 vs, 728 w, 762 s, 776 m, 818 vs, 843 w, 868 w, 892 m, 921 m, 935 vs, 965 m, 1001 w, 1016 w, 1071 w, 1090 w, 1124 m, 1139 vs, 1174 w, 1201 m, 1226 vs, 1259 m, 1286 w, 1305 w, 1320 m, 1364 s, 1385 s, 1416 w, 1454 m, 1502 vs, 1584 w, 1615 m, 1755 w, 1876 w, 2899 s, 2949 vs.

$^1$H NMR ($CDCl_3$, 297 K): $\delta$ = 0.89 (s, 9H, C($CH_3$)$_2$$CH_2$C($CH_3$)$_3$), 1.33 (s, 6H, C($CH_3$)$_2$$CH_2$C($CH_3$)$_3$), 1.48 (d, $J_{HH}$ = 6.7 Hz, 3H, $CH_3$), 1.68 (s, 2H, C($CH_3$)$_2$$CH_2$C($CH_3$)$_3$), 3.99 (q, $J_{HH}$ = 6.7 Hz, 1H, CH), 3.74, 4.13 (2d, $J_{HH}$ = 16.4, 2H, N−$CH_2$−Ar), 4.89, 5.10 (2d, $J_{HH}$ = 10.5 Hz, 2H, O−$CH_2$−N), 6.74 (d, $J_{HH}$ = 8.7 Hz, 1H, Ar), 6.84 (s, 1H, Ar), 7.14 (d, $J_{HH}$ = 8.7 Hz, 1H, Ar), 7.27−7.34 (m, 5H, Ph).

$^{13}$C NMR ($CDCl_3$, 297 K): $\delta$ = 21.4 (1C, NCHPh$CH_3$), 31.4, 31.6, 31.7, 32.3 (7C, C($CH_3$)$_2$$CH_2$C($CH_3$)$_3$), 49.1 (1C, N−$CH_2$−Ar), 56.9 (1C, NCHPh$CH_3$), 57.4 (1C, C($CH_3$)$_2$$CH_2$C-($CH_3$)$_3$), 80.0 (1C, O−$CH_2$−N), 127.1 (1C, *p*-C(Ph)), 127.2 (2C, *m*-C(Ph)), 128.4 (2C, *o*-C(Ph)), 144.6 (1C, *i*-C(Ph)−CH), 115.2, 119.1, 125.1, 125.3, 141.9, 152.2 (6C, Ar).

**Details of X-ray Data Collection and Reduction.** X-ray diffraction data were collected using a KUMA KM4 CCD ($\omega$ scan technique) diffractometer equipped with an Oxford Cryosystem-Cryostream cooler.[9] The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix-least-squares on $F^2$ using SHELXTL Package.[10] Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined. All data (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-719484 (*S*-**1**) and CCDC-719485 (*S*-**1**·2,4-di-*tert*-Bu$C_6H_3$OH). Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (E-mail: deposit@ccdc.cam.ac.uk).

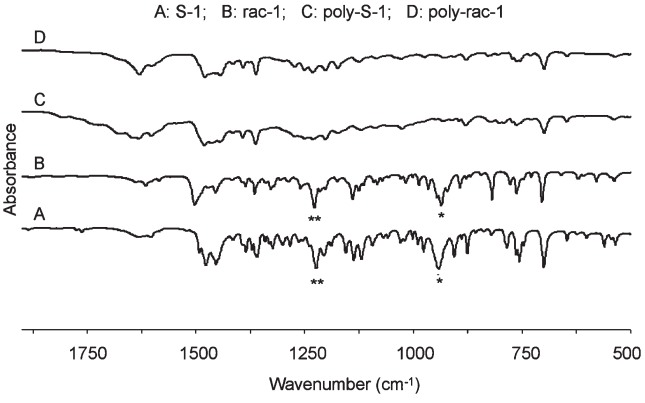
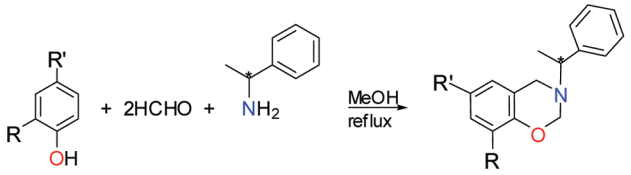



**Figure 1.** FT-IR spectra of *S*-**1** (A), *rac*-**1** (B), poly-*S*-**1** (C), and poly-*rac*-**1** (D) in the 1880−500 $cm^{-1}$ region (∗ - 947 (*S*-**1**) and 951 (*rac*-**1**); ∗∗ - 1223 (*S*-**1**) and 1224 (*rac*-**1**)).

**Scheme 1. Synthesis of *S*-1 and *rac*-1-2**




*S*/*rac*-***1***: R = R' = $^t$Bu

*rac*-***2***: R = H, R' = 1,1,3,3-tetra-methylbutyl

## Results and Discussion

**Monomer Synthesis and Characterization.** Synthetic approaches to 3,4-dihydro-2*H*-1,3-benzoxazines include: Mannich condensation of phenol and a primary amine with formaldehyde,[1] condensation of *o*-hydroxybenzylamine with an aldehyde,[11] rearrangement reactions of 2-(allyloxy) benzylamine with $H_2$/CO in the presence of rhodium catalysts,[12] condensation of 4-substituted phenol with 1,3,5-trimethyl-hexahydro-*s*-triazine in the presence of oxalyl chloride,[13] reaction of 1-(bromomethyl)-2-(chloromethoxy) benzene with primary amines,[14] and dehydratation of *N*-(2-hydroxybenzyl)-3-aminopropanoic acid in the presence of sulfuric acid.[15] Another method to synthesize benzoxazines is a direct *ortho*-metalation[16] for example lithiation of phenols or side-chain lithiation of substituted phenols[17] or *via* copper-catalyzed three-component coupling reactions.[18]

From all these methods Mannich condensation seems to be the most commonly used methodology and the best applicable synthetic strategy for the construction of 1,3-benzoxazines. Hence, according to this method, we have synthesized novel, chiral and racemic benzoxazines *S*-**1**, *rac*-**1**, and *rac*-**2**. Reactions were performed in methanol for about 36 h at the phenol/amine/formaldehyde molar ratio 1:1:2.5. Conversion to analytically pure benzoxazines *S*-**1**

**Table 1. Summary of Crystallographic Data for *S*-1 and *S*-1·2,4-Di-*tert*-Bu$C_6H_3OH$**

| | | |
|---|---|---|
| molecular formula | $C_{24}H_{33}NO$ | $C_{38}H_{55}NO_2$ |
| molecular weight | 351.51 | 557.83 |
| crystal system | orthorhombic | orthorhombic |
| space group | $P2_12_12_1$ | $P2_12_12_1$ |
| temperature of collection (K) | 100(2) | 100(2) |
| cell dimensions (100(1) K) | | |
| *a*, Å | 5.836(3) | 9.005(3) |
| *b*, Å | 12.933(6) | 11.984(3) |
| *c*, Å | 27.760(10) | 31.372(9) |
| *V*, Å$^3$ | 2095.2(16) | 3385.5(17) |
| *Z* | 4 | 4 |
| $d_{calc}$, g/cm3 (100(1) K) | 1.114 | 1.094 |
| $\mu$ mm$^{-1}$ | 0.067 | 0.500 |
| crystal dimensions, mm | 0.60 × 0.20 × 0.20 | 0.60 × 0.40 × 0.30 |
| radiation $\lambda$ | Mo Kα (0.71073 Å) | Cu Kα (1.5418 Å) |
| no. of reflections measured | 14265 | 31482 |
| range/indices (*h*, *k*, *l*) | −7, 7; −16, 16; −19, 36 | −11, 9; −15, 11; −39, 35 |
| $\theta$ limit, deg | 2.71−28.55 | 3.95−75.92 |
| total no. of unique data | 2869 | 6471 |
| no. of observed data, $I > 2\sigma(I)$ | 2253 | 6292 |
| no. of variables | 235 | 507 |
| no. of restraints | 0 | 0 |
| $R_{int}$ | 0.0597 | 0.0397 |
| $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ (all, observed) | 0.0728, 0.0483 | 0.0452, 0.0444 |
| $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w[F_o^4]^{1/2}$ (all, observed) | 0.0842, 0.0894 | 0.1239, 0.1226 |
| absorption correction ($T_{min}$, $T_{max}$) | | analytical (0.892, 0.944) |
| absolute structure parameter | 0(10)[a] | 0.12(19) |
| $\Delta\rho$ (max, min), e/Å$^3$ | 0.16, −0.20 | 0.34, −0.26 |

[a] Since the compound is a weak anomalous scatterer, the absolute structure parameter is meaningless (the s.u. of the Flack parameter is large).

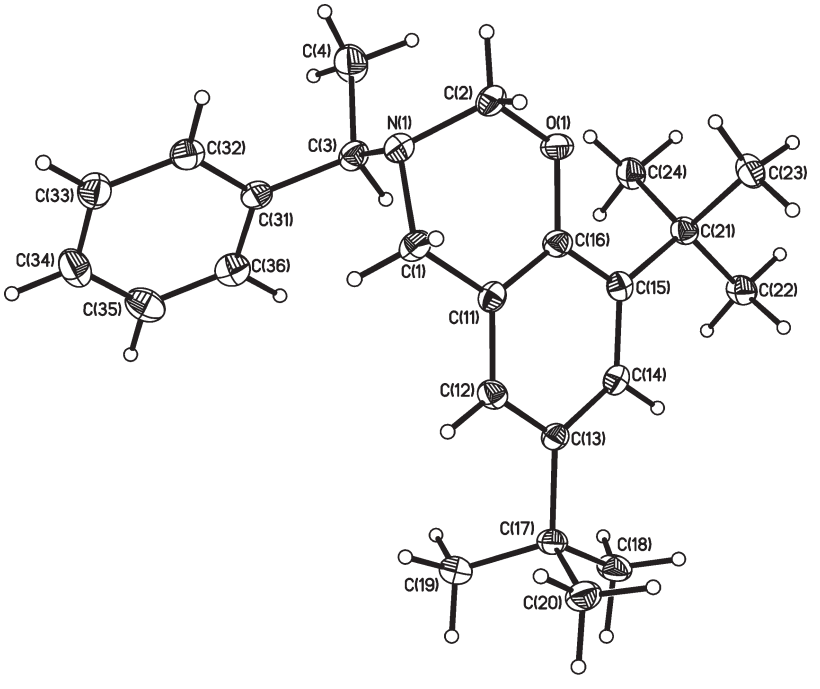



**Figure 2.** Molecular structure of *S*-**1** with atom-labeling.

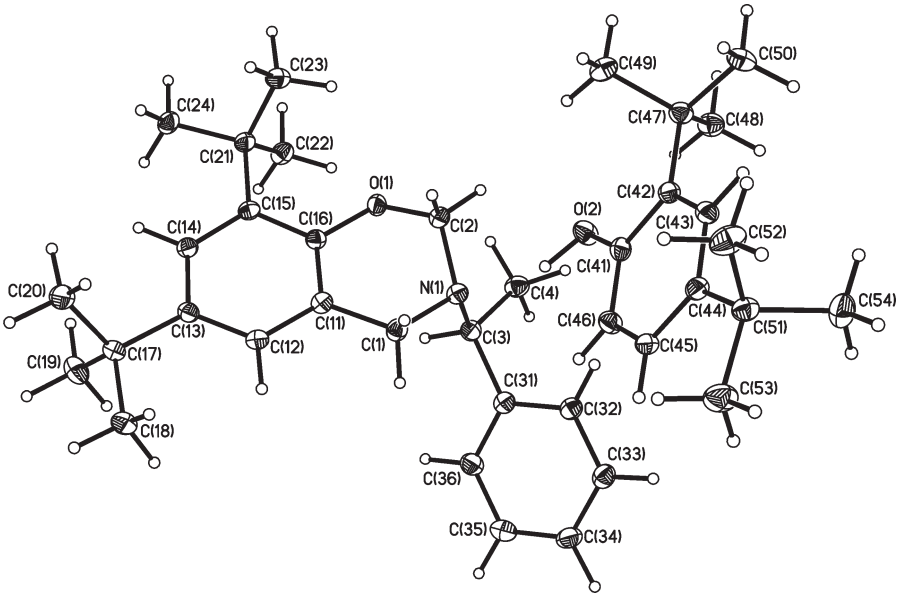



**Figure 3.** Molecular structure of *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ with atom-labeling.

and *rac*-**1**-**2** proceeded in high 81−85% yields as shown in Scheme 1. The compounds were characterized by elemental analysis, FT-IR, $^1H$ and $^{13}C$ NMR spectroscopy and, for *S*-**1**, by X-ray crystallography.

As shown in Figure 1, parts A and B, the IR spectra of *S*/*rac*-**1** are similar and exhibited bands at 947 and 1223 $cm^{-1}$ (*S*-**1**) and 951 and 1224 $cm^{-1}$ (*rac*-**1**) characteristic for benzoxazine type structure (bands are indicated in Figure 1 by an asterisk). As expected, these bands disappears in each of polymer spectrum, demonstrating the effective opening of the oxazine rings (Figure 1, parts C and D). The IR spectrum for *rac*-**2** also contains associated with benzoxazine structure fingerprints at 935 and 1226 $cm^{-1}$. These bands are absent in the IR spectrum of the corresponding poly-*rac*-**2**. Additionally the characteristic band at 3346 $cm^{-1}$ is detected for poly-*rac*-**2** due to OH group in polymer chain, typical for phenolic-type-structure (see Scheme 3).

The $^1H$ NMR spectra for *S*/*rac*-**1** are identical and informative as to formation of oxazine ring. The diagnostic signals of diastereotopic methylene protons of the two -$CH_2$- groups from the heterocycle give at room temperature dublets at 3.85 and 4.14 for N−$CH_2$-Ar and at 4.77 and 5.03 ppm for O−$CH_2$-N. The methylbenzyl substituent on nitrogen atom is also evidenced by a dublet at 1.46 ($CH_3$) and a quartet at 3.97 (CH) ppm. The aromatic protons from nitrogen substituent appeared as multiplet between 7.24 and 7.40 ppm. The resonances at 49.4 and 79.4 ppm in the $^{13}C$ spectrum of *S*/*rac*-**1** monomer are also diagnostic for benzoxazine systems.

The mass spectrum for *S*-**1** exhibited an intense signal of parent molecular ion consistent with target benzoxazine.

The FT-IR, $^1H$ and $^{13}C$ NMR spectra of *rac*-**2** also fully confirmed formation of the benzoxazine structure.

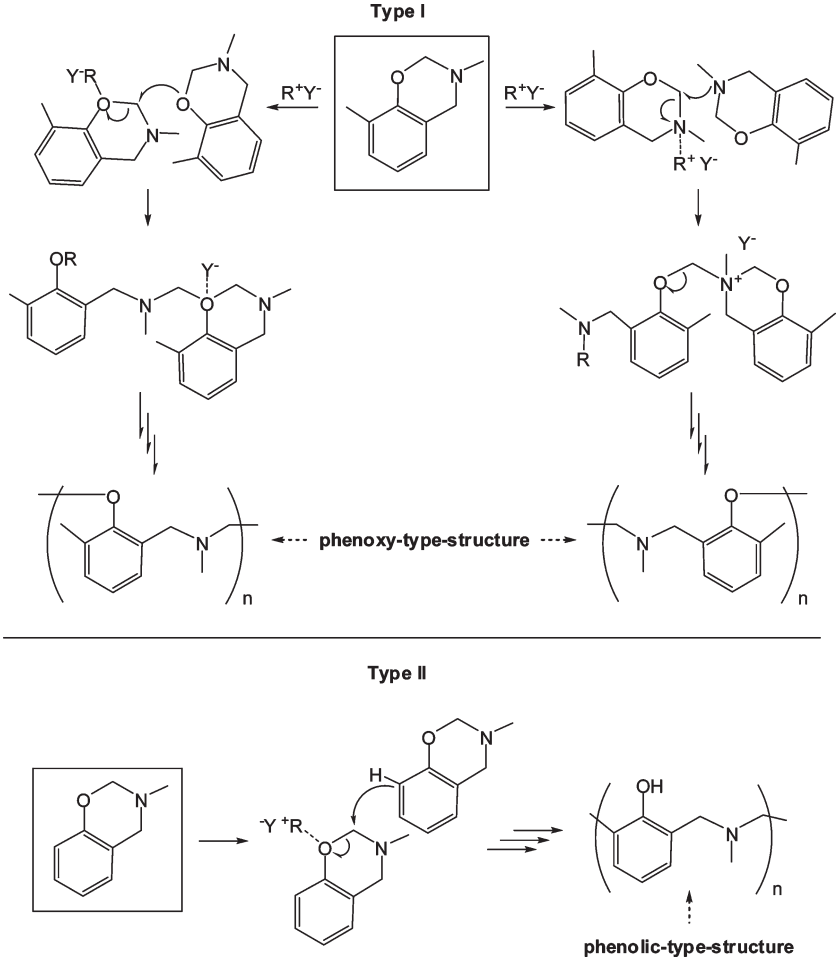
**Crystallographic Studies.** Compound *S*-**1** appeared to be resistant for benzoxazine ring-opening *via* further reaction with an excess of 2,4-di-*tert*-butylphenol. Addition of the phenol resulted in hydrogen-bond assisted adduct *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$.

Colorless block-shaped crystals of *S*-**1** and *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ were crystallized from cold methanol. The detailed structures of both compounds were established by X-ray crystallography as described in Table 1. Figures 2 and 3 show their ORTEP views and the selected interatomic distances and bond angles are summarized in Table 2. As can easily be noticed, the structures of both compounds are almost identical in terms of bond lengths and angles

**Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles for *S*-1 and *S*-1·2,4-Di-*tert*-$BuC_6H_3OH$**

| | *S*-**1** | *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ |
|---|---|---|
| O(1)−C(2) | 1.452(2) | 1.4321(17) |
| O(1)−C(16) | 1.388(2) | 1.3871(17) |
| N(1)−C(1) | 1.481(3) | 1.4814(19) |
| N(1)−C(2) | 1.437(3) | 1.4495(19) |
| N(1)−C(3) | 1.493(3) | 1.4912(19) |
| C(1)−C(11) | 1.518(3) | 1.518(2) |
| C(3)−C(4) | 1.536(3) | 1.522(2) |
| C(3)−C(31) | 1.517(3) | 1.532(2) |
| N(1)−C(1)−C(11) | 110.87(18) | 113.30(12) |
| N(1)−C(2)−O(1) | 114.27(18) | 113.64(12) |
| N(1)−C(3)−C(4) | 110.9(2) | 111.63(13) |
| N(1)−C(3)−C(31) | 109.19(18) | 108.28(12) |
| O(1)−C(16)−C(11) | 120.46(19) | 119.96(13) |
| O(1)−C(16)−C(15) | 118.20(19) | 118.01(13) |
| C(1)−N(1)−C(2) | 106.08(16) | 107.13(12) |
| C(1)−N(1)−C(3) | 110.77(18) | 111.50(11) |
| C(1)−C(11)−C(12) | 121.6(2) | 120.21(13) |
| C(1)−C(11)−C(16) | 119.5(2) | 120.60(13) |
| C(2)−N(1)−C(3) | 114.71(18) | 115.49(12) |
| C(2)−O(1)−C(16) | 115.98(17) | 112.58(11) |
| C(4)−C(3)−C(31) | 110.51(18) | 111.23(12) |
| C(3)−C(31)−C(32) | 121.1(2) | 120.32(13) |
| C(3)−C(31)−C(36) | 120.7(2) | 121.38(14) |
| N(1)−C(1)−C(11)−C(12) | 151.4(2) | 169.72(13) |
| N(1)−C(1)−C(11)−C(16) | −24.6(3) | −15.55(19) |
| N(1)−C(3)−C(31)−C(32) | −53.5(3) | −60.32(17) |
| N(1)−C(3)−C(31)−C(36) | 127.1(2) | 120.37(15) |
| C(1)−N(1)−C(2)−O(1) | −65.2(2) | −64.98(16) |
| C(1)−N(1)−C(3)−C(4) | 172.07(18) | 167.34(12) |
| C(1)−N(1)−C(3)−C(31) | −66.0(2) | −69.89(14) |
| C(1)−C(11)−C(16)−O(1) | −0.9(3) | 6.9(2) |
| C(1)−C(11)−C(16)−C(15) | 176.39(19) | −173.87(14) |
| C(2)−N(1)−C(1)−C(11) | 54.7(2) | 41.66(16) |
| C(2)−N(1)−C(3)−C(4) | 52.0(2) | 44.75(17) |
| C(2)−N(1)−C(3)−C(31) | 174.01(17) | 167.53(12) |
| C(2)−O(1)−C(16)−C(11) | −6.1(3) | −26.14(18) |
| C(3)−N(1)−C(1)−C(11) | −70.4(2) | −85.60(15) |
| C(3)−N(1)−C(2)−O(1) | 57.4(2) | 59.90(17) |
| C(4)−C(3)−C(31)−C(32) | 68.7(3) | 62.70(19) |
| C(4)−C(3)−C(31)−C(36) | −110.7(3) | −116.61(16) |
| C(16)−O(1)−C(2)−N(1) | 41.0(3) | 57.55(17) |

**Scheme 2. Mechanisms of Polybenzoxaxine Syntheses Proposed by Wang and Ishida (type I, Phenoxy Type Structure; Type II, Phenolic-Type Structure)**

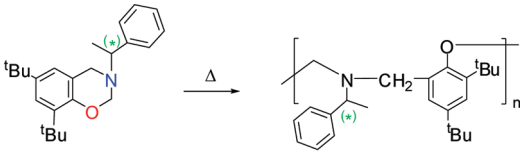



but significantly differ as to the conformation of the oxazine rings.

In both compounds, the oxazine ring crystallizes in preferential (also for further polymerization) distorted half-chair conformation with the $\theta$ and $\varphi$ parameters of 127.5 (2) and 289.2(3)° for *S*-**1** and 134.38(10) and 259.4(2)° for *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$. Nevertheless, a closer look at the oxazine torsion angles shows important differences. All the within-the-oxazine-ring torsion angles C(11)−C(16)−O(1)−C(2) −6.1(3)° for *S*-**1** and −26.14(18)° for *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$, C(16)−O(1)−C(2)−N(1), (41.0(3)° and 57.55(17)°), O(1)−C(2)−N(1)−C(1) (−65.2(2)° and −64.98 (16)°), C(2)−N(1)−C(1)−C(11) (54.7(2)° and 41.66(16)°), N(1)−C(1)−C(11)−C(16) (−24.6(3)° and −15.55(19)°), and C(1)−C(11)−C(16)−O(1) (−0.9(3)° and 6.9(2)°) differ significantly. In consequence, the position of the methylene carbon C(2) and nitrogen N(1) in relation to the plane defined by aryl C(11) to C(16) atoms also changes essentially in both compounds. The position of both atoms on the opposite sides of this plane is believed to be an important factor that promotes polymerization. In *S*-**1**, the C(2) atom lies almost in this plane (deviated by −0.021 Å) while the nitrogen N(1) is above it by 0.727 Å. The same atoms are more leaned out of the plane in *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ where C(2) remains −0.5328 and N(1) 0.1138 Å out of it.

**Reactivity and Polymerization.** One of the most important reactions of benzoxazines is the phenol-induced ring-opening reaction which was first reported by Burke.[19] It has been found that aminoalkylation of phenols occurred

**Scheme 3. Synthesis of poly-*S*/*rac*-1**




*S*/*rac*-**1** poly-*S*/*rac*-**1**

preferentially at their free *ortho* position to form a Mannich base bridge structure. Ring-opening mechanism by protonation of the oxygen atom to form an iminium ion, followed by electrophilic aromatic substitution was then proposed by Dunkers and Ishida.[20] According to this, we have approached the direct reaction of *S*/*rac*-**1** and 2,4-di-*tert*-butylphenol in 1:1 molar ratio. Unfortunately, we have not observed formation of the appropriate amino-*bis*-phenol. Changes in reaction conditions (temperature, time, substrates ratios and type of phenol) constantly gave analogous results, which in case of 2,4-di-*tert*-butylphenol was the adduct *S*/*rac*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ (structure of *S*-**1**·2,4-di-*tert*-$BuC_6H_3OH$ is described above).

In the next thrust, we approached the polymerization of the obtained benzoxazines. One of the typical polymerization processes is the thermal ring-opening (ROP) of a benzoxazine monomer in the absence of a catalyst and without generating any byproduct.[21] Wang and Ishida proposed two different mechanisms of such process depending on

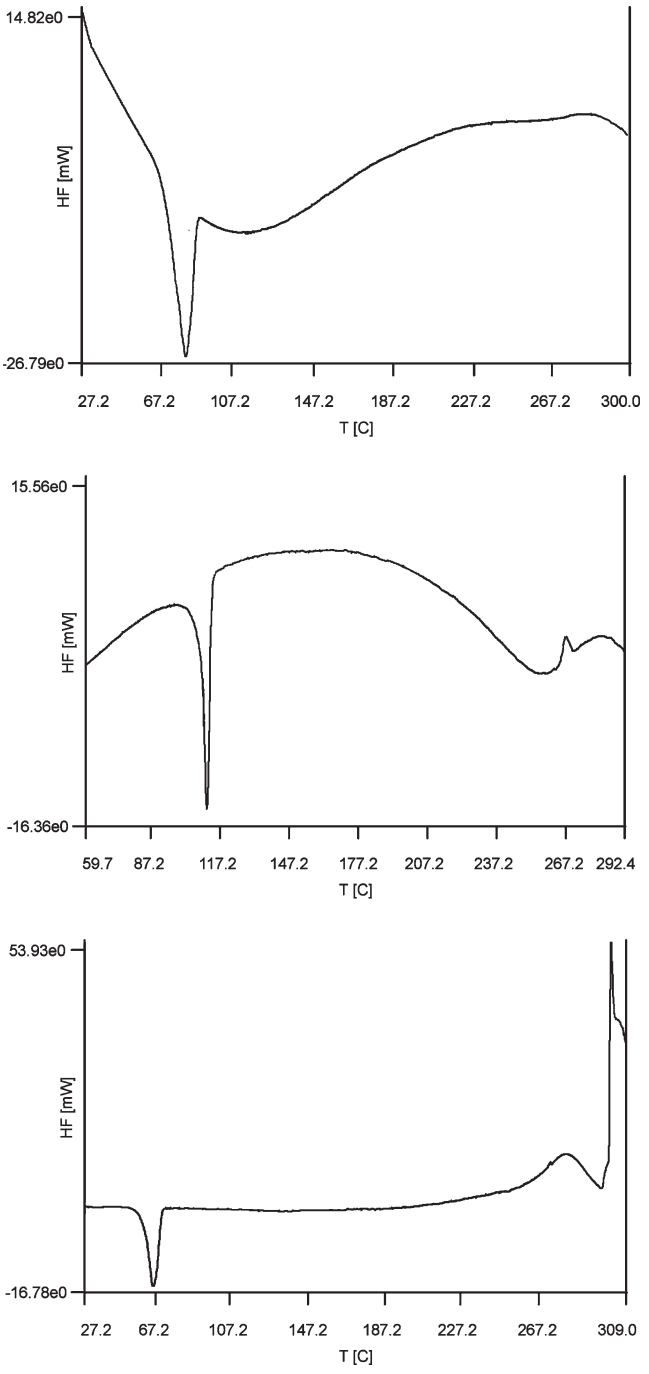



**Figure 4.** DSC for monomers: S-**1** (top), *rac*-**1** (middle), and *rac*-**2** (bottom). Calculated heats of reaction (J/g) and $T_{pol}$ (°C) are as follows: *S*-**1**, 5.63 and 291; *rac*-**1**, 5.42 and 263; *rac*-**2**, 81.8 and 294.

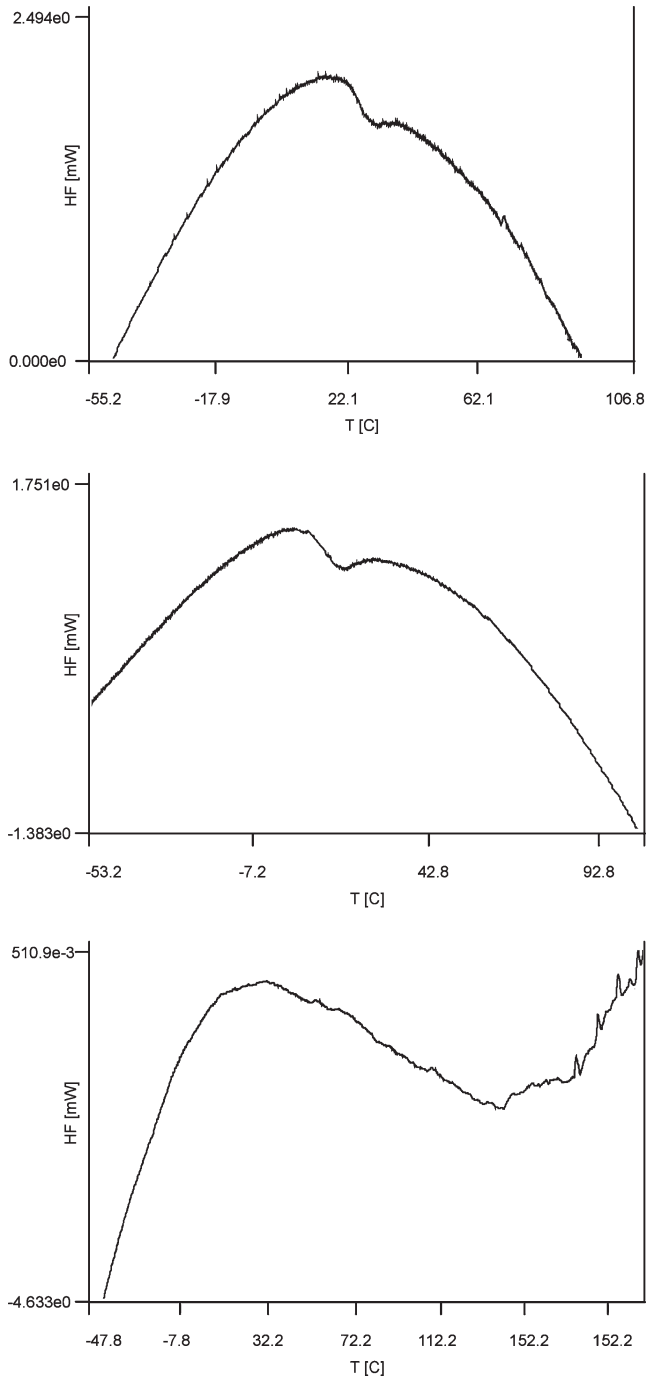



**Figure 5.** DSC (second scan) of thermally polymerized *S*-**1** (top), *rac*-**1** (middle), and *rac*-**2** (bottom) for $T_g$ determination.

the position of substituents in the aromatic ring of the phenolic moiety (Scheme 2) which results in two kinds of polymers.[22] The formation of type I polymer proceeds via insertion of monomers through the reaction between the cyclic tertiary oxonium ion and the oxygen of another oxazine ring. In the alternative route nitrogen acts as an initiation center as well as propagation site. The type II polymer is formed by incorporation of monomers through the reaction of unsubstituted *ortho* position of the phenolic moiety.

As mentioned above, monomers *S*/*rac*-**1** and *rac*-**2** were subjected for thermal polymerization as shown in Scheme 3.

DSC was employed to monitor the polymerization reactions and to measure the polymer glass transition temperature ($T_g$). Polymerization was achieved by heating the benzoxazine monomers (in a DSC instrument) at 20 °C/min in nitrogen atmosphere from 25 to 300 °C. Figure 4 shows resulted DSC curves, each exhibiting two main thermal transitions. The first one of endothermal type was assigned to the melting process and the other was assigned to the ROP of the benzoxazine ring.

The resulting polymers are solids at room temperature and were characterized by $T_g$. A second DSC scan (Figure 5), carried out on curied samples from −60 to 100 °C revealed $T_g$ of 31 °C for *S*-**1**, 19 °C for *rac*-**1**, and 138 °C for *rac*-**2**.

In accordance with what was reported in the literature, we postulate the formation of polybenzoxazines by ring cleavage of the $CH_2$−O bond as illustrated in Scheme 2.

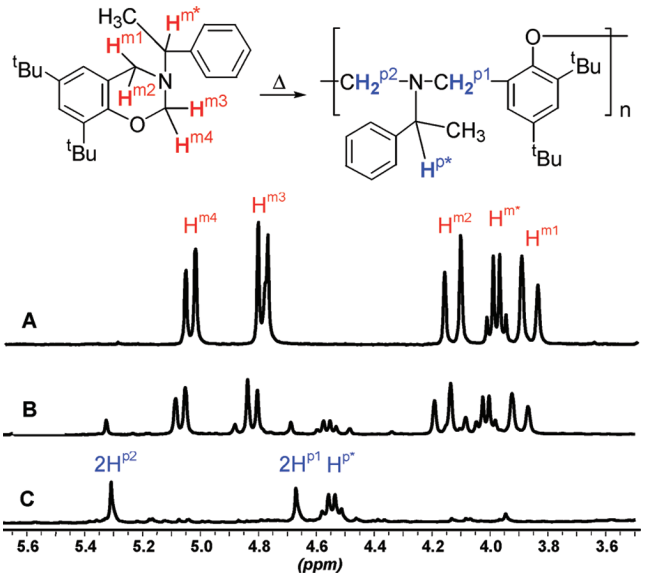



**Figure 6.** $^1$H NMR spectra in the region of methine (monomer, m*; polymer, p*) and methylene (monomer, m; polymer, p) protons of thermally polymerized *S*-**1**: (**A**) benzoxazine monomer *S*-**1** at room temperature; (**B**) poly-*S*-**1** formed after heating at 260 °C; (**C**) poly-*S*-**1** formed after heating at 300 °C.

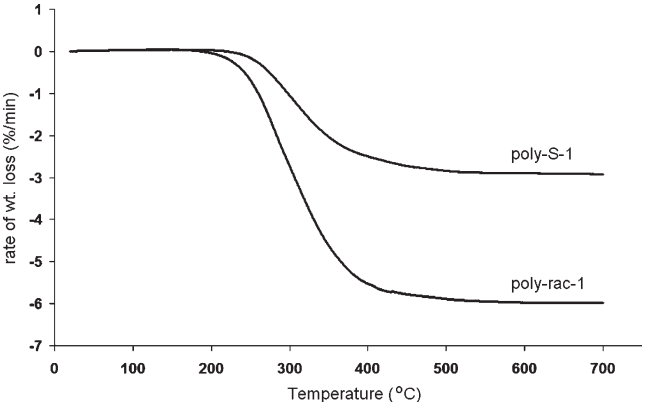



**Figure 7.** TGA of poly-*S*/*rac*-**1**.

The polymerization process was observed by temperature $^1$H and $^{13}$C NMR analysis as shown in Figure 6.

Inspection of $^1$H NMR spectrum of poly-*S*-**1** reveals two resonances at 4.66 and 5.30 ppm with equal integrated intensities. This implies that two different methylene groups exist in repeating unit of polybenzoxazine (see Scheme 2). Particularly interesting are methyl and methine protons which are observed as dublet at 1.63 ppm ($J$ = 6.7 Hz; not shown in Figure 5) and quartet at 4.53 ppm ($J$ = 6.7 Hz) for poly-*S*-**1**. The resonances of the corresponding $CH_3$ and CH protons for poly-*rac*-**1** appeared in the $^1$H NMR in the same positions but as multiplets. These spectrum pattern may came from the isotactic structure of the poly-*S*-**1**.

The results of TGA experiments of these polymers are shown in Figure 7. It can be noticed that polymers remain fairly stable up to 200 °C for poly-*S*-**1** and to 180 °C for poly-*rac*-**1**.

On the basis of the results from spectroscopic (IR, NMR) analysis of obtained polymers, polybenzoxazines (poly-*S*/*rac*-**1**) form a phenoxy-type-structure (Scheme 2). On the other hand, polymerization of benzoxazine with free *ortho* position *rac*-**2** gave polymer (poly-*rac*-**2**) with a phenolic-type structure.

## Conclusions

In summary, we have synthesized three new benzoxazines *S*/*rac*-**1** and *rac*-**2** by standard Mannich condensation. One of the monomers possessed chiral-at-carbon S-α-3-methylbenzyl substituent at the nitrogen atom. Compounds were characterized by spectroscopic methods and in case of *S*-**1** and its 2,4-di-*tert*-Bu$C_6H_3$OH containing polymorph also by X-ray crystallography. The compounds were found to thermally polymerize, possibly *via* $CH_2$−O bond cleavage, at temperatures 263−293 °C to give polymers of type II.[2] Their chemical structure was characterized by NMR spectroscopy and DSC. Comparison of polybenzoxazines derived from the chiral and racemic monomers *S*/*rac*-**1** show small but noticeable differences. The polymerization temperatures for *S*-**1** and *rac*-**1** differ by 29 °C (*S*-**1**, 291 °C; *rac*-**1**, 263 °C). Interestingly, both polymers exhibit significantly improved thermal properties which are expressed by low $T_g$ values of 19 and 31 °C. Such low values are not common and were observed for instance in a polymer obtained from cardanol-based benzoxazine monomer.[23] It should be underlined that the temperature for *S*-**1** is higher by 12 °C, which ought to be associated with stereoregularity of the polymer resulted from enantiomerically pure monomer. What is also interesting, the TGA showed the polymer derived from *S*-**1** to exhibit much smaller rate of weight loss indicating enhanced thermal stability of the product. Next, properties of poly-*S*-**1** and poly-*rac*-**1** were compared with those of poly-*rac*-**2**, which characteristics is free (proton occupied) *ortho* position of the phenyl ring. Although its $T_{pol}$ of 294 °C is similar to those for *S*-**1** and *rac*-**1**, the much higher $T_g$ suggests that a polymer of type II[2] formed in this case.

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