

SYNTHESIS OF NOVEL BENZOXAZINE HAVING VINYL GROUP AND COPOLYMERIZATION WITH VINYL MONOMERS

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Abstract

A novel benzoxazine having vinyl group, namely P-4va, was prepared from phenol, formaldehyde and 4-vinylaniline. The chemical structure of P-4va was confirmed by FT-IR and ¹H NMR analyses. The polymerization behavior was investigated by differential scanning calorimetry (DSC). Exothermic peak of P-4va appeared at 209 °C in the DSC measurement due to the chain polymerization of the vinyl group and the ring-opening of benzoxazine, which occurred at the same temperature range. Thermal cure of P-4va afforded PP-4va that has glass transition temperature (T_g) at 244 °C and char yield above 48%, exhibiting that the thermal properties of PP-4va is higher than those of a typical polybenzoxazine without vinyl group. Radical polymerization of P-4va and copolymerization with styrene (St) and methyl methacrylate (MMA) were carried out using 2,2'-azobisisobutyronitrile as the initiator, affording homopolymer and copolymers bearing benzoxazine units as the pendant. Further heat treatment of the copolymers at 240 °C afforded cured copolymers with T_g above 300 °C and high char yield, indicating that the copolymers serve as high-molecular-weight precursors of polybenzoxazine.

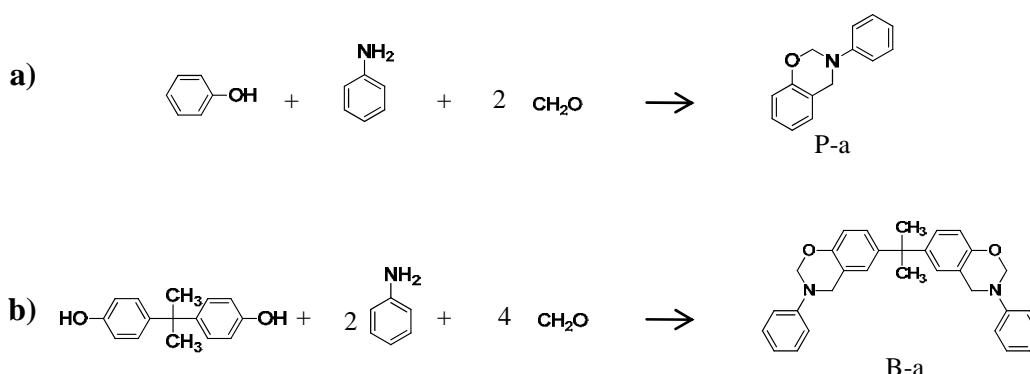
Keywords: Benzoxazine, Radical polymerization, Ring-opening polymerization, Thermoset, Vinyl group

Introduction

The conventional phenolic resins have been widely used in various applications, such as construction, household facilities and electrical appliances, because of their outstanding characteristic properties, such as good mechanical properties, excellent heat resistance, flame retardancy and dielectric properties. Another attractive advantage of phenolic resins is relatively low cost because they are synthesized from inexpensive starting materials. Nevertheless, the traditional phenolic resins brought many drawbacks such as brittleness, poor shelf lives, strong acid catalysts necessary for polymerization and releasing by-products during curing process such as water and ammonia. Additionally, the volatilization of starting materials during heat treatment causes huge volumetric shrinkage and forms micro voids in the cured resins.

The novel type of phenolic resins namely polybenzoxazine has been developed to overcome the drawbacks associated with the conventional phenolic thermosets. Typical benzoxazines, P-a and B-a, are simply prepared from either phenol or bisphenol-A with primary amine and formaldehyde (Scheme 1) [1-4]. The manner of the benzoxazine synthesis offers the molecular design flexibility for the cyclic monomers. As a novel type of phenolic resin, polybenzoxazines have the advantages of the conventional phenolic resins such as excellent heat resistance, flame retardancy and low dielectric properties. Furthermore, polybenzoxazines have many unique characteristics which are not found in the traditional phenolic resins including near zero shrinkage upon curing, good mechanical and physical properties, low water absorption, as well as low surface free energy. The curing process of benzoxazine resins through heat treatment does not need harsh catalysts,

does not generate by-products, thus the polymerization of benzoxazines is considered as a green process, and some of them have T_g even higher than the curing temperature.



Scheme 1. Syntheses of P-a (a) and B-a (b)

Nevertheless, their thermal properties are not high enough to withstand in harsh condition of applications, and the brittle property as a nature of thermosets limits their application. The performance enhancement of the polybenzoxazines has been conducted by various approaches. The designing of novel monomers by introducing cross-linkable units into the benzoxazine moiety is based on the concept to suppress the volatilization of aniline fragment during thermal decomposition of the polybenzoxazines. Various functional groups such as nitrile [5,6], ethynyl [7,8], propargyl [9] and allyl groups [10] have been introduced into the benzoxazine structure (Figure 1). As the results, the thermal properties of polybenzoxazines were increased because of the increase of cross-link density in network structures of polybenzoxazine due to the reactions of the functional groups in addition to the ring opening polymerization. The synthesis of high molecular weight precursors containing cyclic benzoxazine group in the backbone is another effective approach to enhance both the thermal and the mechanical properties of polybenzoxazines [11-13]. The polybenzoxazines from the high molecular weight precursors exhibited significantly improved toughness and high T_g due to the long linear backbone and high crosslink density. Polymer alloys [14-17] and organic-inorganic hybrid materials [18-23] are also effective approaches for the performance enhancement of polybenzoxazines.

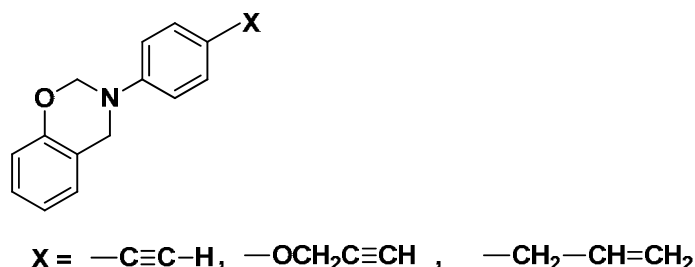
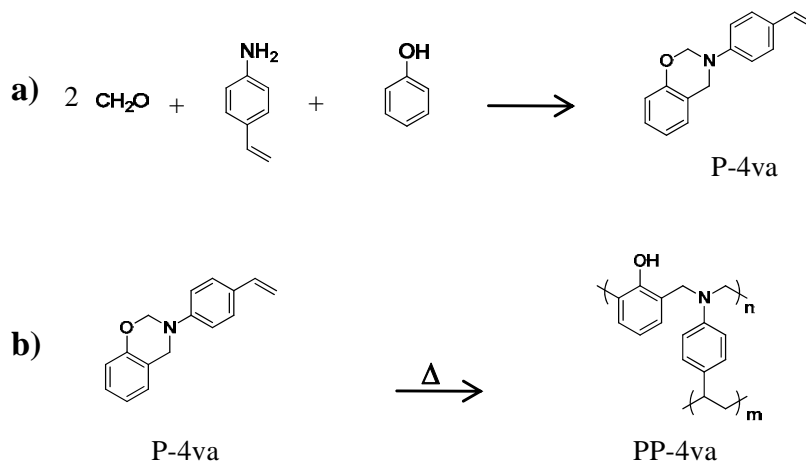


Figure 1. Chemical structure of benzoxazines containing cross-linkable units

In this study, we prepared a novel benzoxazine having vinyl group, namely P-4va, as shown in Scheme 2a. The introducing of the vinyl group into the typical benzoxazines is aiming to enhance the thermal properties of polybenzoxazines by increasing the cross-link density through the chain polymerization of vinyl group and the ring-opening

polymerization reaction of benzoxazine (Scheme 2b). Furthermore, homopolymerization of P-4va and copolymerization with vinyl monomers using a radical initiator were examined as a novel approach for the preparation of high molecular weight polybenzoxazine precursors.



Scheme 2. Syntheses of P-4va and PP-4va

Experimental

Reagents

Phenol (99 %) was received from Sigma-Aldrich Chemistry Company. Bisphenol-A (99 %), paraformaldehyde (94 %), 4-vinylaniline (95 %), and 2,2'-azobisisobutyronitrile (AIBN) (98 %) were obtained from Tokyo Chemical Industry Co., LTD. Tetrahydrofuran (THF) (99.5 %), chloroform (99 %) and benzene (99.5 %) were purchased from Wako Pure Chemical Industries, Ltd. Styrene (St, > 99 %), and methyl methacrylate (MMA, > 98 %) obtained from Wako were repeatedly washed with aqueous NaOH, then purified by fractional distillation under reduced nitrogen pressure, dried over CaH_2 , and vacuum-distilled just prior to polymerization.

Preparation of P-4va

The synthetic procedure of P-4va is as follows: Into 30 mL of chloroform, paraformaldehyde (0.96 g, 25 mmol) and then 4-vinylaniline (1.57 g, 12.5 mmol) were added, and the mixture was stirred at room temperature for 10 min. Phenol (1.19 g, 12.5 mmol) was then added, and reaction temperature was raised and stirred under reflux for 48 h. The reaction mixture was filtered to remove any insoluble product, washed with 0.1 N aqueous hydrochloric acid and then 0.5 N aqueous NaOH three times each. Thereafter, the chloroform solution was washed with distilled water several times until the water layer reached the neutral phase. The organic layer was dried over anhydrous magnesium sulfate (MgSO_4) for one night. After filtering off MgSO_4 , chloroform was removed under vacuum. P-4va was obtained as a reddish powder (1.6 g, 53% yield).

Preparation of the Cured Film (PP-4va)

P-4va was dissolved in THF (50 wt% solution). The reddish brown solution was cast on a glass substrate pretreated with dichlorodimethylsilane. The cast film was thermally treated under air oven at 50 °C for 12 h, and then at 100, 150, 200 and 240 °C for 1 h each, affording a reddish transparent polybenzoxazine film. The thickness of the films can be controlled in the range of 40 - 45 µm.

Radical Copolymerization of P-4va with St or MMA

Under nitrogen atmosphere, AIBN (16.42 mg, 0.1 mmol) was dissolved in benzene (2 mL), followed by adding monomer mixtures of P-4va with St or MMA (total monomer concentration: 5 mmol/L). The solutions were degassed by freeze-thawing. The radical polymerization was carried out at 60 °C. After 24 h, the polymerization was terminated by cooling to 0 °C. The reaction mixtures were concentrated under reduced pressure at room temperature, and then poured into large amount of MeOH. The brown precipitate was collected by filtration, and dried under vacuum to give the copolymers.

Curing of Copolymer

Copolymers were dissolved in THF to prepare 30 wt% solutions by stirring at 80 °C for 3 h. The obtained reddish brown solutions were cast on glass substrates. The solvent was removed in air oven at 50 °C for 12 h. The copolymer films were further cured at 100, 150, 200 and 240°C for 1 h each, affording reddish transparent polybenzoxazine films. The thickness of the films was controlled to be 45-75 µm.

Measurements

NMR spectra were measured with a Varian Mercury 300 instrument (300 MHz for ¹H). IR spectra were recorded on a JASCO model FT/IR-420 spectrophotometer. Differential scanning calorimetry (DSC) was performed with Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen. Size exclusion chromatography (SEC) was measured with JASCO instrument with UV-2075 (254 nm) or refractive index detectors. Chloroform was used as the eluent at a flow rate of 1.0 mL/ min at 40 °C. Two polystyrene gel columns (TSK-GEL MULTIPORE HLX-M) were used. Thermogravimetric analysis (TGA) was measured with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5 °C/min under argon. Dynamic viscoelastic measurements were conducted on ORIENTEC automatic dynamic viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C/min.

Results and Discussion

Preparation of P-4va

For the preparation of benzoxazines, a method using solvent (solvent method) and a method without using solvent (solvent-less method) are known [24]. When solvent-less method was employed at 100 °C for the preparation of P-4va, the mixture of phenol, 4-vinylaniline and formaldehyde turned to reddish color in a few minutes and the viscosity of the mixture increased with reaction time. We obtained reddish solid that is insoluble in many solvents such as THF, dimethylformamide, CHCl₃, ether and toluene. This may be due to the rapid formation of networks by the chain polymerization of vinyl group and the ring opening reaction. It was suggested that the solvent-less method cannot be applied to form the benzoxazine having vinyl group.

On the other hand, solvent method was successfully applied for the preparation of P-4va. Various solvents were employed to synthesize P-4va such as diethyl ether, MeOH, toluene, THF, chloroform and 1,4-dioxane at 50 °C. Among the solvents, 1,4-dioxane and chloroform were found to be suitable to prepare P-4va with moderate yield (~50 %). In this study, chloroform was used because it is easy to remove. The formation of P-4va in chloroform under reflux was monitored by ^1H NMR analyses after 6, 12, 24, 36, 48 and 56 h. We observed the increase of oxazine peaks along with the decrease of triazine, and the appropriate reaction time was determined to be 48 h. P-4va was obtained as reddish powder in 53 % yield.

The chemical structure of P-4va was confirmed by using ^1H NMR and IR spectra. ^1H NMR spectrum of P-4va in Figure 2 shows the characteristic resonances of the vinyl group as two doublets at 5.11 and 5.59 ppm, corresponding to the protons of $-\text{C}=\text{CH}_2$ (a) and as a quartet at 6.62 ppm corresponding to $-\text{CH}=\text{}$ (b), respectively. The two singlet resonances at 4.63 ppm (c) and 5.36 ppm (d) were assigned to the typical characteristic protons in oxazine ring, $-\text{C}-\text{CH}_2-\text{N}-$ and $-\text{O}-\text{CH}_2-\text{N}-$, respectively. The multiplet at 6.60 – 7.42 ppm was assigned to the protons of aromatic ring.

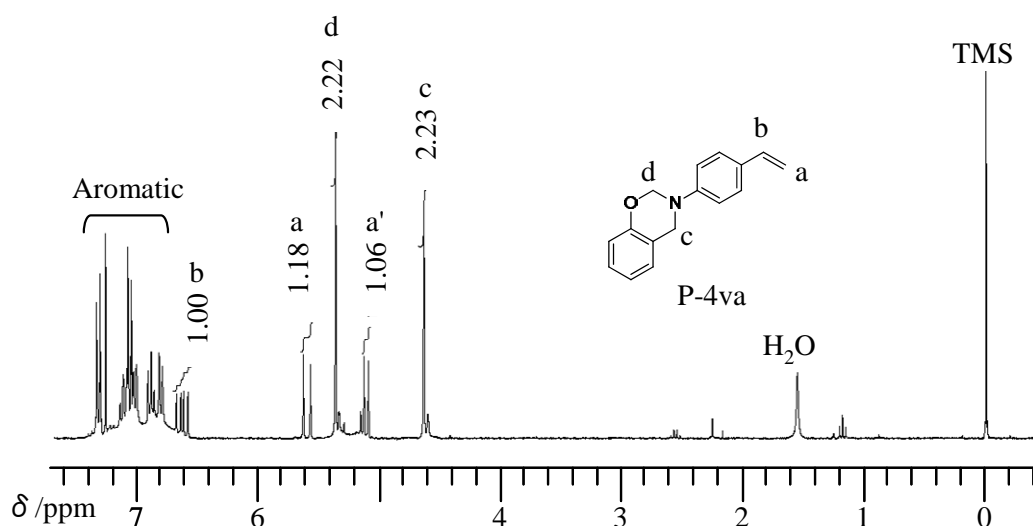


Figure 2. ^1H NMR spectrum of P-4va

IR spectra of benzoxazines are shown in Figure 3. Typical absorption bands for the benzoxazines are observed at 1495, 1370, 1229, 1035 and 946 cm^{-1} , corresponding to the di-substituted benzene rings (for P-a), CH_2 wagging, Ar-O-C antisymmetric stretching, C-O-C symmetric stretching and vibration mode of cyclic substituted benzene rings, respectively. The appearance of new characteristic absorption band at 1511 cm^{-1} can be assigned to the di-substituted benzene of 1,4-benzene from 4-vinylaniline. The absorptions at 900 and 990 cm^{-1} are assigned to the C-H out of plane deformation vibration of vinyl group.

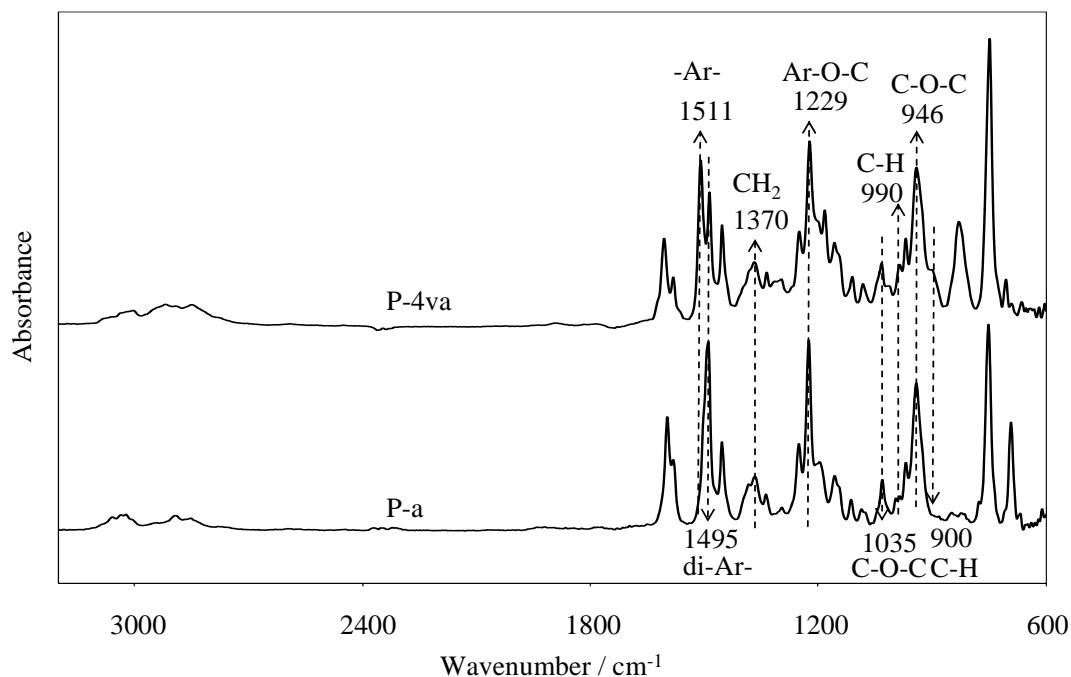


Figure 3 IR spectra of P-a and P-4va

Curing Behavior of P-4va

The curing behavior of the novel benzoxazine, P-4va, was compared with the typical benzoxazine, P-a, using DSC (Figure 4). The DSC of P-a showed a sharp exothermic peak with maximum at 223 °C, corresponding to the ring-opening polymerization reaction of P-a. While, P-4va showed a broad exothermic peak at lower temperature range than P-a, with maximum at 209 °C. The peak broadening implies that the chain polymerization of vinyl group and the ring-opening polymerization of benzoxazines occurred at the same temperature range. This is supported from the higher amount of exotherm, 49 kJ/mol for P-4va against 37 kJ/mol for P-a.

The progress of curing of P-4va was investigated by DSC. Figure 5 shows DSC curves of P-4va after each cure stage. The decrease of the exothermic amount is clearly observed with the increase of curing temperature. The exotherm disappeared after curing at 240 °C, indicating the completion of cross-link reaction.

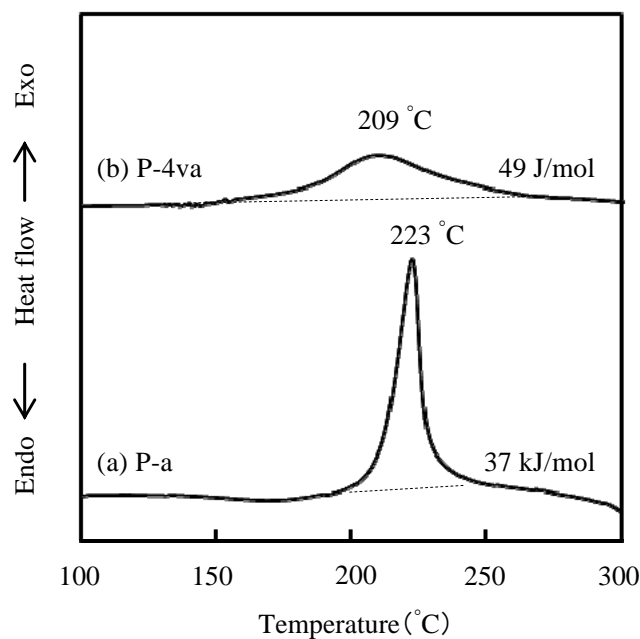


Figure 4. DSC curves of P-a and P-4va.

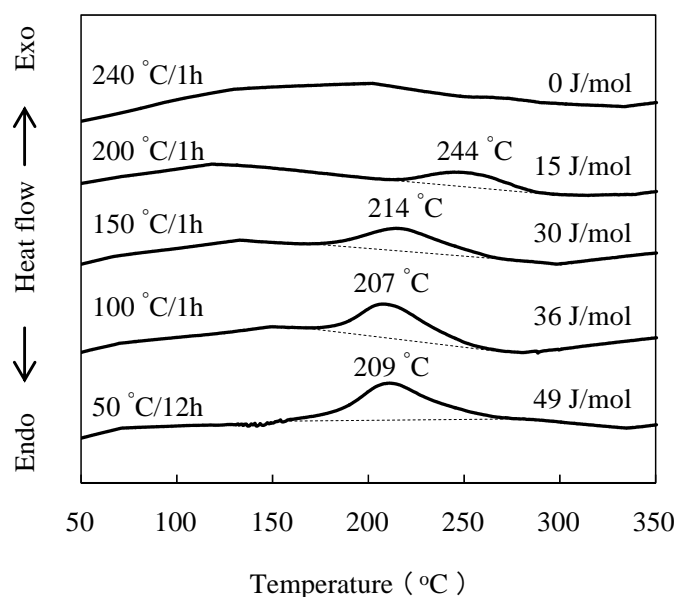


Figure 5. DSC curves of P-4va after cure at 50, 100, 150, 200, and 240 °C

IR spectra of P-4va after each cure stage, as shown in Figure 6, exhibited that, with the increase of curing temperature, the absorption bands of the vinyl group at 900 and 990 cm^{-1} , as well as the oxazine and substituted benzene rings at 1495, 1370, 1229, 1035 and 946 cm^{-1} decreased and finally disappeared after the curing at 240 °C. Close look at the IR spectra shows that the characteristic absorption bands of the vinyl group disappeared after 150 °C cure, and the absorptions of benzoxazine finally disappeared after cured at 240 °C.

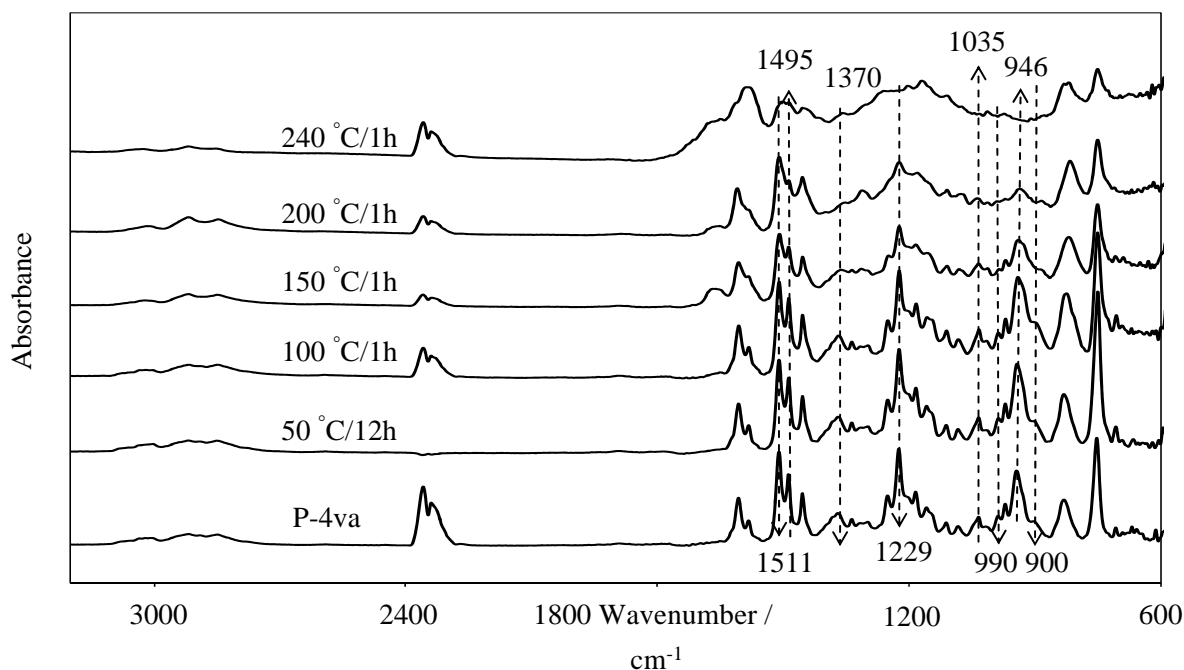


Figure 6. IR spectra of P-4va after cure at 50, 100, 150, 200, and 240 °C

Properties of the Cured PP-4va Film

A reddish transparent polybenzoxazine film, PP-4va, was obtained by casting a THF solution of P-4va on a glass plate, followed by curing up to 240 °C. The thermal properties of the polybenzoxazine films were investigated by dynamic mechanical analysis (DMA). As shown in Figure 7, the glass transition temperature (T_g) of a typical polybenzoxazine film (PP-a) was 172 °C and 175 °C from E'' and $\tan \delta$, respectively. While, T_g of PP-4va was found at 230 °C and 244 °C from E'' and $\tan \delta$, respectively. The significant enhancement in T_g of PP-4va suggests that the formation of increased network structure for PP-4va was occurred, due to the chain polymerization of the vinyl group and the ring opening polymerization reaction of benzoxazines.

The thermal stability of polybenzoxazine having vinyl group was investigated by TGA under argon atmosphere, as shown in Figure 8. The initial weight loss temperature of PP-a at 5 and 10 % (T_5 and T_{10}) were at 319 and 358 °C, respectively. While, the T_5 and T_{10} of PP-4va increased up to 355 and 378 °C, respectively. The char yield of PP-4va at 850 °C was 48 %, also higher than that of PP-a, 46 % at 850 °C. The TGA results suggest that the aniline moiety was anchored into the network structure by the chain polymerization of the vinyl group.

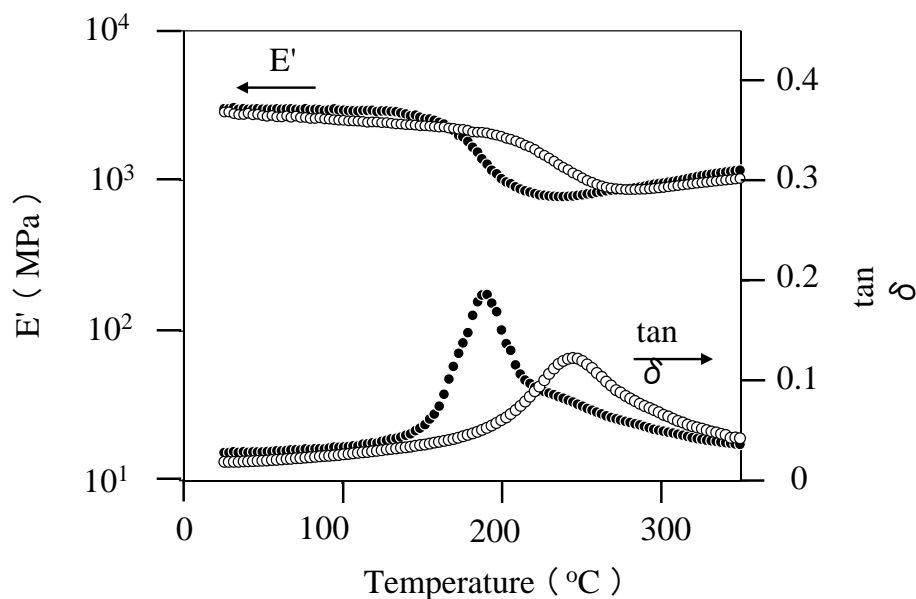


Figure 7. DMA of PP-a (●) and PP-4va (○)

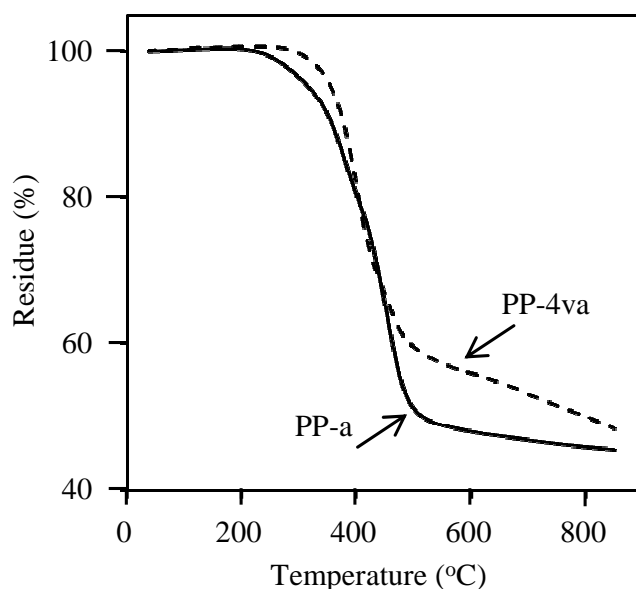
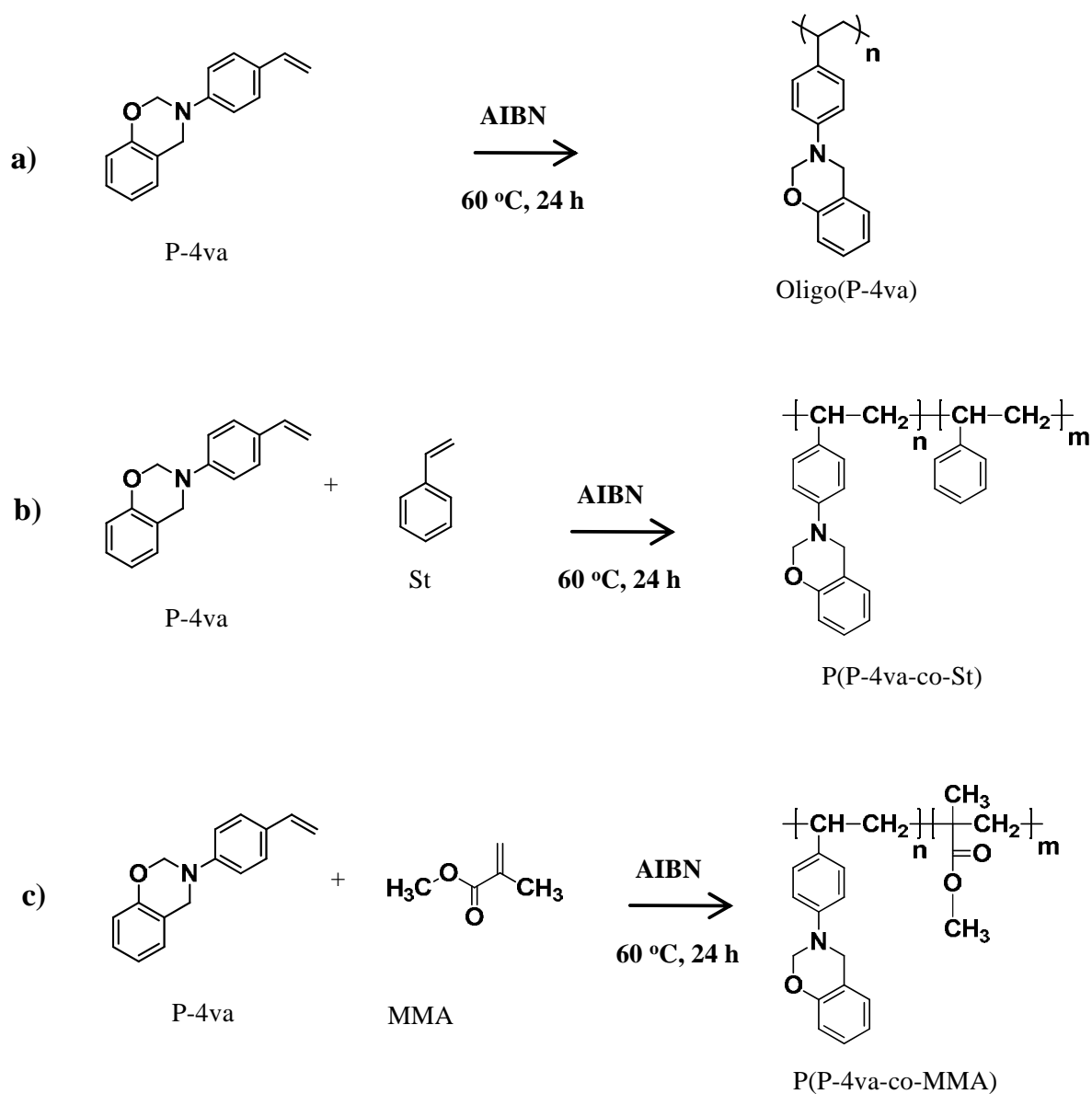


Figure 8. TGA curves of PP-a and PP-4va

Radical Copolymerization of P-4va with St and MMA

We investigated radical polymerizability of the vinyl group of P-4va. We expected that linear-type polymers containing benzoxazine unit as the pendant can be obtained by the radical polymerization as shown in Scheme 3. Radical homopolymerization of P-4va with AIBN was carried out in benzene at 60 °C. After 24 h, a MeOH-insoluble material was obtained in 64 % yield. However, the molecular weight determined by SEC was considerably low ($M_n = 650$, Table 1), indicating low radical homopolymerizability of P-4va. Figure 9a shows ^1H NMR spectrum of the oligomer (oligo(P-4va)). The oligomer did not show olefinic proton signals, confirming that the radical initiation proceeded. Moreover, typical protons of benzoxazine were observed at 4.53 ppm (Ar- $\text{CH}_2\text{-N}$) and 5.32 ppm (O- $\text{CH}_2\text{-N}$). These results indicate that the benzoxazine unit remains even after the radical reaction.



Scheme 3. Radical polymerization of P-4va (a) and copolymerization with styrene (b) and with MMA (c)

Table 1. Radical Polymerization of P-4va with St or MMA in Benzene at 60 °C, 24 h.

Code	Monomer ^a		Composition ^b		Yield ^c (%)	M _w ^d	M _n ^d
	Feed (mol%)		Found (mol%)				
	P-4va	St or MMA	f ₁	f ₂			
Oligo(P-4va)	100	-	100	-	64	1070	650
PSt	-	100	-	100	52	33100	18000
PMMA	-	100	-	100	73	47800	26500
P(P-4va/St)	50	50	23	77	60	8300	2800
P(P-4va/MMA)	90	10	83	17	57	1900	1050

^a [I] = AIBN = 0.1 mmol, [M] = [P-4va+St/MMA] = 10 mmol.

^b Identified from ¹H NMR spectra.

^c Products after purification in MeOH.

^d Identified by SEC measurements.

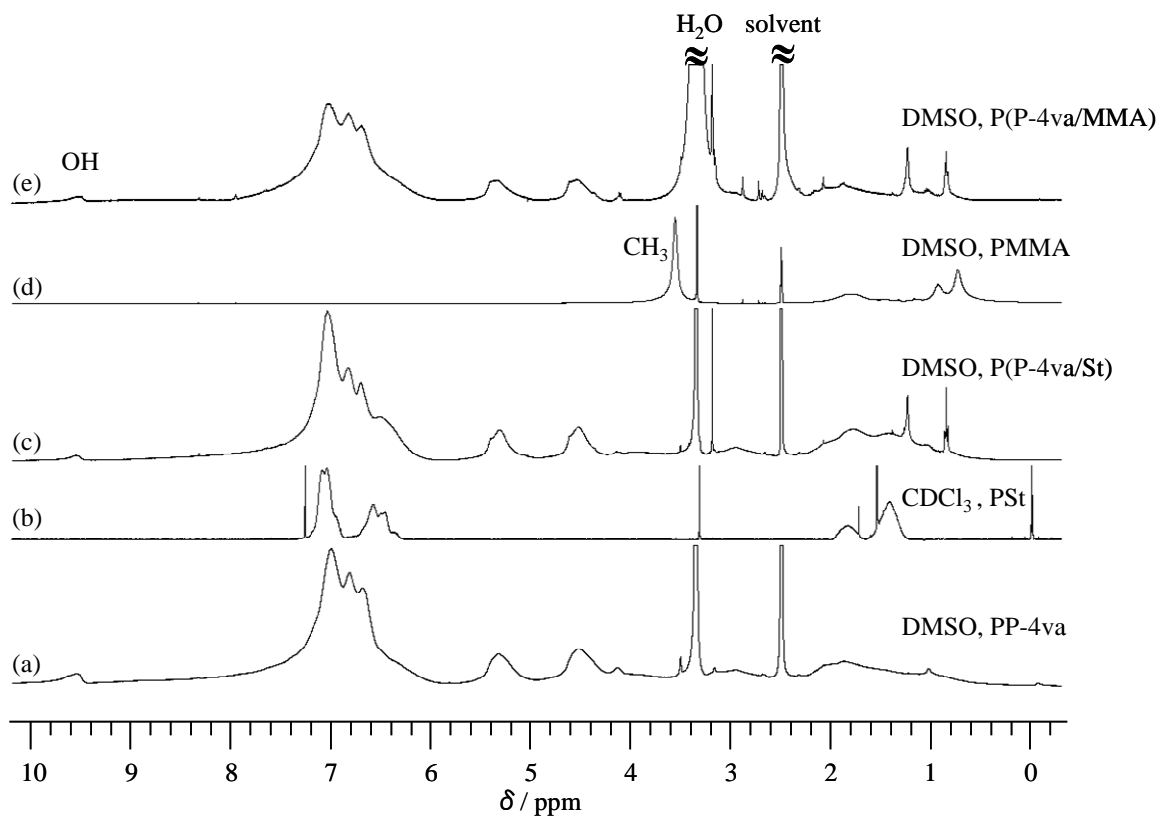


Figure 9. ¹H NMR spectra of oligo(P-4va) (a), PSt (b), P(P-4va/St) (c), PMMA (d) and P(P-4va/MMA) (e).

Next, radical copolymerization with styrene (St) was carried out (Scheme 3). Copolymerization of P-4va and styrene with AIBN gave a polymeric product with 60 % yield (Table 1). The M_n of the copolymer was estimated to be 2800 by SEC, which is higher than that of the homopolymer. ^1H NMR spectrum of the copolymer is shown in Figure 9c. The characteristic signals of benzoxazine units were observed (4.5-5.5 ppm), indicating that the benzoxazine unit was introduced into the polystyrene chain as the pendant.

Similarly, copolymerization of P-4va and MMA with AIBN was carried out in benzene at 60 °C for 24 h. As shown in Table 1, yield of the copolymer was 57 % and M_n of the copolymer was estimated to be 1050 by SEC. ^1H NMR spectrum of the copolymer (Figure 9d) shows the characteristic signals of benzoxazine units, indicating the introduction of benzoxazine unit into the PMMA chain as the pendant.

Curing Behavior of Copolymers

The curing behavior of oligo(P-4va) and copolymers was characterized by DSC. As shown in Figure 10, oligo(P-4va) gave broad exothermic peak with maximum at 235 °C and 19 kJ/mol as exothermic heat, showing that the ring-opening polymerization of benzoxazine unit occurred during the DSC measurement. The ring-opening polymerization behavior was also observed for P(P-4va/St) and P(P-4va/MMA) copolymers as the exothermic peaks at 240 and 241 °C, respectively, with the exothermic heat of 25 and 22 kJ/mol, respectively. These results clearly indicate that oligo(P-4va) and the copolymers serve as polybenzoxazine precursors.

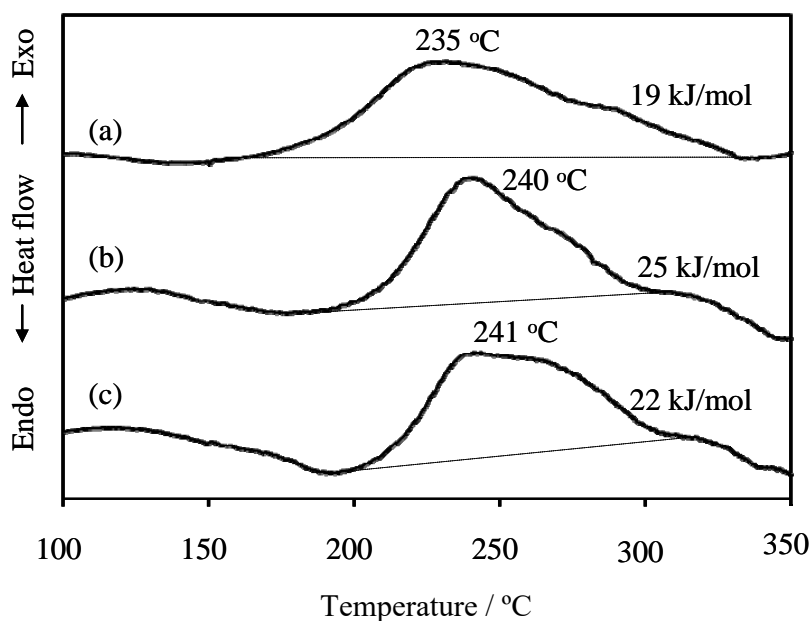


Figure 10. DSC curves of oligo(P-4va) (a), P(P-4va/St) (b) and P(P-4va/MMA) (c)

Properties of Polybenzoxazines from Oligo(P-4va) and Copolymers

Oligo(P-4va), P(P-4va/St), and P(P-4va/MMA) were thermally cured up to 240 °C on glass plates. Free-standing polybenzoxazine films were obtained from oligo(P-4va), P(P-4va/MMA), and P(P-4va/St). Though oligo(P-4va) and P(P-4va/St) gave very brittle cured films, P(P-4va/MMA) gave cured film that is tough enough for the mechanical property measurement.

The viscoelastic property of the cured P(P-4va/MMA) film was characterized by DMA (Figure 11). The T_g of PP-4va from the maxima of E'' and $\tan \delta$ was, as mentioned before,

230 and 244 °C, respectively. While T_g of P(P-4va/MMA) from the maxima of E'' and $\tan \delta$ was observed at 286 and 307 °C, respectively, which is ca. 60 °C increase from the PP-4va without PMMA. Interestingly, the introduction of PMMA into the network structure of polybenzoxazine significantly enhanced T_g .

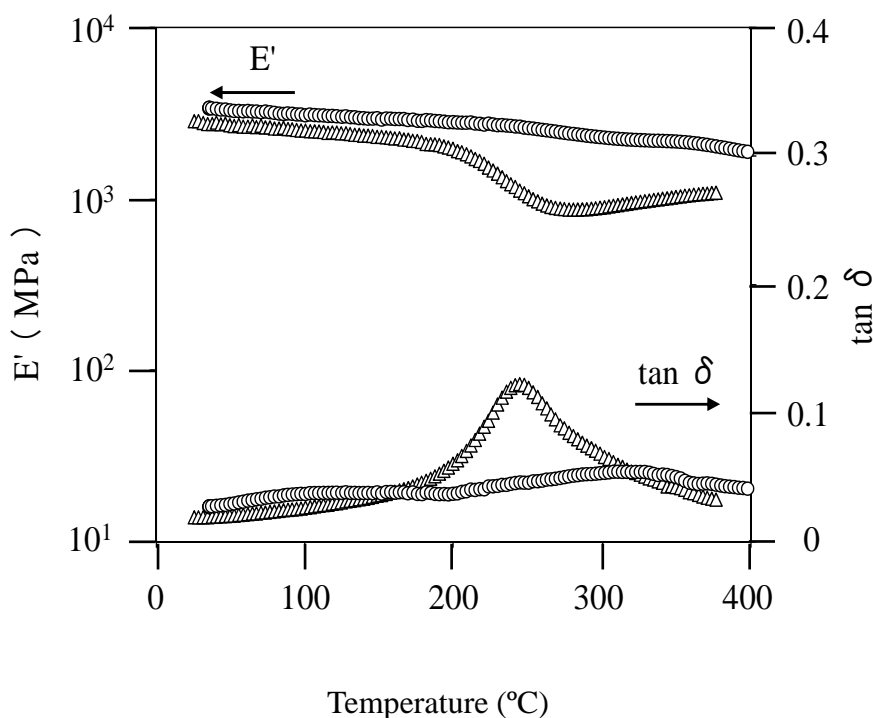


Figure 11. Viscoelastic properties of PP-4va (Δ) and P(P-4va/MMA) (O).

The thermal stability of P(P-4va/St) and P(P-4va/MMA) was investigated by TGA under argon atmosphere (Figure 12). For oligo(P-4va), T_5 and T_{10} were estimated to be 364 and 394 °C, respectively (Figure 12a). The char yield at 850 °C was as high as 53 %. On the other hand, T_5 and T_{10} for PSt were 346 °C and 372 °C, respectively. The T_5 and T_{10} for PMMA were determined to be 332 and 343 °C, respectively. Both PSt and PMMA decomposed completely at ca. 400 °C. In contrast, P(P-4va/St) shows T_5 and T_{10} at 345 °C and 378 °C, respectively, with as high as 45 % of char yield at 850 °C. Meanwhile, T_5 and T_{10} of P(P-4va/MMA) were determined to be 346 and 373 °C, respectively, with the char yield as high as 44 %, which is almost same as P(P-4va/St). From the TGA measurement, it can be concluded that the thermal stability of copolymers was almost similar to that of oligo(P-4va). The char yields of the copolymers were lower than that of oligo(P-4va) due to the lower heat resistance of PSt and PMMA component.

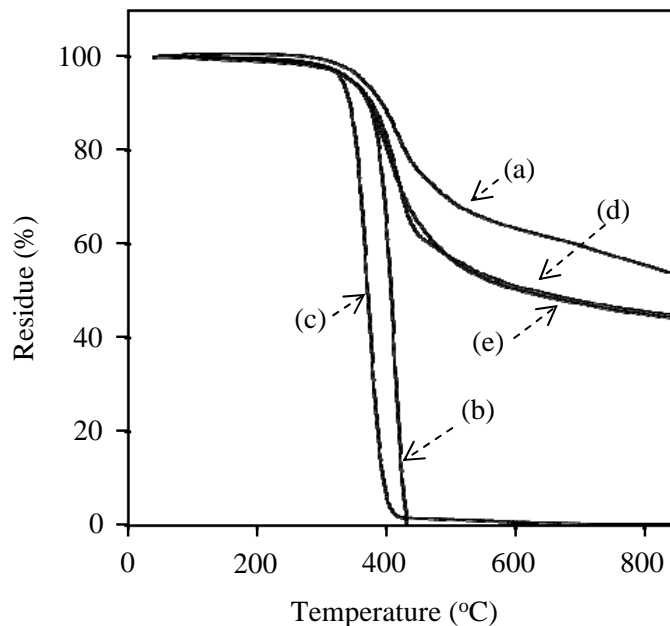


Figure 12. TGA curves of the oligo(P-4va) (a), PSt (b), PMMA (c), P(P-4va/St) (d), and P(P-4va/MMA)

Conclusions

Novel benzoxazine having vinyl group, P-4va, was successfully synthesized. The film of polybenzoxazine having vinyl group was obtained easily by casting P-4va solution on glass substrate and curing up to 240 °C for 1 h. The reddish transparent polybenzoxazine films exhibited significantly improved thermal properties such as high T_g and improved thermal stability, due to the formation of increased network structures of polybenzoxazine by the additional chain polymerization of the vinyl group. Moreover, radical polymerization of P-4va and copolymerization with vinyl monomers gave linear-type oligomer and copolymers having benzoxazine unit as the pendant, which serve as high-molecular-weight precursors of polybenzoxazine. By using P-4va, the benzoxazine unit may be introduced easily into many type of vinyl polymers.

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