Formation of 4,4′-Thiodiphenol-Modified Epoxy Resins Monitored by GPC and MALDI–TOF Mass Spectrometer

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ABSTRACT: Reaction intermediates in the reaction of 4,4′-thiodiphenol (TDP) and Epikote 828 (E 828) for the formation of the diglycidyl ether of bisphenol A (DGEBA) epoxy copolymers (ETP) were determined by using a combination of two methods, viz. gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization/time-of-flight (MALDI–TOF) spectrometer. This combination provides the measurement of true molecular weight and distribution, which in turn, enables the structural identification of intermediates and determination of their respective contents. The content of ideal component, the E 828-(TDP-E 828)$_n$, $n = 1$ in ETP copolymer, was found to be 2.3, 13.0, and 34.4% for ratios of 1/1, 1/2, and 1/3 of TDP and E 828, respectively. The ETP epoxy copolymers also exhibited thermal improvement over E 828 and other DGEBA resins of the E 1000 series, as indicated by their higher glass transition temperature (T_g) in differential scanning calorimeter (DSC) and better thermostability in thermogravimetric analysis (TGA) measurements. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1621–1631, 1998

Key words: true M_w; epoxies; MALDI–TOF; GPC

INTRODUCTION

Polyphenylene sulfide (PPS) has been known to possess several useful characteristics, such as thermal stability and good mechanical properties, which have been attributed to the existance of phenylenesulfide linkage in its structure.[1–3] The introduction of 4,4′-thiodiphenol (TDP) as the alternate dihydroxyarene (DHA) besides bisphenol F (BPF) or bisphenol sulfone (BPS) also may impart these properties to the epoxy system. The addition of TDP as a part of the main chain of the modified epoxy resin (abbreviated as ETP) may afford some flexibility to the system, needed to offset the inherited brittleness from epoxy's self-crosslinking process during the thermal curing with amine curative. The divalent —S— linkage is expected to be more flexible than the —SO_2— linkage in BPS or the —$C(CH_3)_2$— linkage in bisphenol A (BPA), yet TDP may provide the thermal stability with aryl groups in the structure of the modified epoxy resins.[4–8]

Recently, a combination of the GPC and the matrix-assisted laser desorption ionization/time-of-flight (MALDI–TOF) mass spectrometer as a method to monitor the copolymerization[9–12] has been shown to yield superior results over the use of their GPC or MALDI–TOF alone.[13–16] This combined method correlates the quantitative distribution data from GPC with the true molecular weight (mass) obtained from MALDI–TOF spectrometer. With this method, the structures and contents of various intermediates in the reaction can be determined. The MALDI–TOF analysis not only provides the true molecular weights in Dalton, but also offers molecular standards for

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molecular calibration. Thus, the combined use of these instruments affords true molecular data for the varieties of polymers.[9–12] Unlike data obtained with the use of the relative molecular weights of polystyrene (PS) standards for the GPC analysis, there is no need to speculate the molecular weights of the reaction intermediates. Notably, it is particularly futile to attempt to describe the formation of copolymer with structural uncertainties for the pertinent reaction intermediates.

The purpose of the present investigation was twofold: to use the combination of GPC and MALDI–TOF methods to monitor and identify the reaction intermediates in the reaction process, and to find the optimum conditions for formation of TDP-modified epoxy resin, minimizing the formation of other undesirable higher homologs.

EXPERIMENTAL

Materials

Epoxy resins of DGEBA (Epikote 828, 1001, and 1004) were procured from Shell Oil Co., locally, and were used directly without further purification. 4,4'-Thiodiphenol (TDP), 2,5-dihydroxybenzoic acid (DHB), and sinapinic acid (SA) were purchased from Aldrich Co. Tetrahydrofuran (THF) was purchased from J. T. Baker.

General Procedure for the Epoxy Resin Preparation

Three ETP resins were prepared from the reaction of E 828 with TDP with in one-to-one, -two, and -three molar ratios, respectively, with constant stirring, at 130°C for 10 h under inert atmosphere. Each of the aliquots was taken from the solution and passed through a PTFE filter and collected in the vials at appropriate intervals during the reaction, and THF was added latter. The specimens were examined by GPC or MALDI–TOF.

Procedures for Use of Combined GPC and MALDI–TOF Methods

The GPC measurement unit was equipped with Physical Spectra P1000 HPLC system, wherein four columns of size 300 × 7.7 mm (with porosity 100, 500, 1000, 10000 Å) with Phenogel-10 from Phenomenex and a Spectra 100 UV spectrometer operating at 254 nm were employed for the measurements. THF was used as mobile phase with a flow rate of 1 mL/min at ambient temperature.

The fractionates of the selected fragments of global GPC curves were collected with a fraction collector of GILSON FC-205 system and the solutions of these fractionates, after appropriate runs (12–16 runs), were subjected to the following uses: (1) the fractionates of the sample in collected solution were subjected to MALDI–TOF analysis for determination of the true molecular weight instead of mass. The use of fragments for this purpose allows achieving better accuracy, due to its narrow distribution of mass. (2) A portion of the collected solution was reinjected into the column to check the elution time. (3) A spike method[18] in which a series of the fractionates corresponding to different elution times was added individually to the original solution, so as to verify the elution time of the fractionate from which it was collected. These fractionates with the verified elution times and known molecular weights may then be used as standards for calibration to determine the true molecular weight and its distribution. (4) A series of 10 PS standards (M_w = 400, 580, 680, 1680, 2350, 3600, 9000, 110,000, 240,000, and 470,000) were used to establish a calibration curve for log (molecular weight) vs. elution time for obtaining the PS-based relative M_w for comparison.

The MALDI–TOF mass spectrometer is HP G2025A, incorporating a 337 nm nitrogen laser with desorption/ionization pulse width duration of 3 ns and an electron multiplier detector, was used in this study. The instrument was operated in positive ion reflection mode with an accelerating potential of +28 kV. The mass scale was calibrated using peptide standard with matrix of sinapinic acid (SA). For each sample, a 2,5-dihydroxybenzoic acid (DHB) was used as the matrix, and an average of 150 laser shots was taken. Careful optimization of the laser power was required to operate at the threshold energy.

Infrared Measurements (IR)

The IR measurements on ETP copolymers were performed on a Jasco IR-700 spectrophotometer. A small amount of sample was dissolved in an appropriate solvent and then cast on NaCl plate before taking the IR measurement.

^{1}H-NMR and ^{13}C-NMR Measurements

Structural data of the hydrogen and carbon atoms, through individual chemical shifts, were obtained by ^{1}H-NMR and ^{13}C-NMR, respectively. The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AM-300 WB FT-NMR at the NSC Instrument Lab.

Determination of Epoxy Equivalent Weight (EEW)

The determination of EEW was also used for monitoring the reaction. A HCl/pyridine method[17] was used for EEW determination. The average value of EEW was obtained and based on four to six samples.

Glass Transition Temperature (T_g) Measurement

The T_g data was determined from the midpoint of the curve in the second run of the thermogram with a Du Pont 9000 DSC instrument. The DSC thermogram of both uncured resins as well as cured specimens were recorded at a scanning speed of 10°C/min in the temperature range of −50–200°C.

Thermogravimetric Analysis (TGA)

A Perkin-Elmer TGS-2 instrument was used for TGA measurements of the ETP-system copolymers. A 6–7 mg sample was used for this purpose, and the measurements were carried out under nitrogen atmosphere at a heating rate of 10°C/min from temperature of 50 to 800°C.

Preparation of ETP Epoxy Copolymer

Synthesis of TDP/E 828 in 1/2 ratio (ETP-1–2) is illustrated here as an example of the preparation of ETP copolymer. The syntheses was carried out at 130°C in a 2000-mL three-neck round-bottomed flask, equipped with a reflux condenser and mechanical stirrer. The reaction mixture was then charged with TDP (218 g, 1 mol) and E 828 (754 g, 2 mol). The crude product was washed with chloroform to remove the unreacted TDP. The following procedures were adapted for the product analysis.

The infrared (IR) spectrum, of the product cast on NaCl plate, exhibited absorptions at 3450 cm^{-1} (—OH), 1378 cm^{-1} [—$(CH_3)_2C$—], 911 cm^{-1} (oxirane), and 700–600 cm^{-1} [—C—S—]. The ^{1}H-NMR spectrum ($CDCl_3$) exhibited peaks (δ) at 7.24, 6.81 ppm [—S—*phenyl*-], 7.12, 7.10, 6.81, 6.79 ppm [—$C(CH_3)_2$—*phenyl*-], 3.33 ppm [oxirane for (—O—C*H*—)], 2.88, 2.73 ppm [oxirane for (—O—CH_2)], 1.62 ppm [—C(CH_3)$_2$—]. The ^{13}C-NMR spectrum ($CDCl_3$) showed major peaks (δ) at 157.77, 165.13, 132.70, 115.35 ppm [—S—*phenyl*-], 156.26, 143.60, 127.96, 127.74, 113.94, 113.86 ppm [—$C(CH_3)_2$—*phenyl*—], 50.19, 44.77 ppm [*oxirane*], 41.69, 30.97 ppm [—$(CH_3)_2C$—].

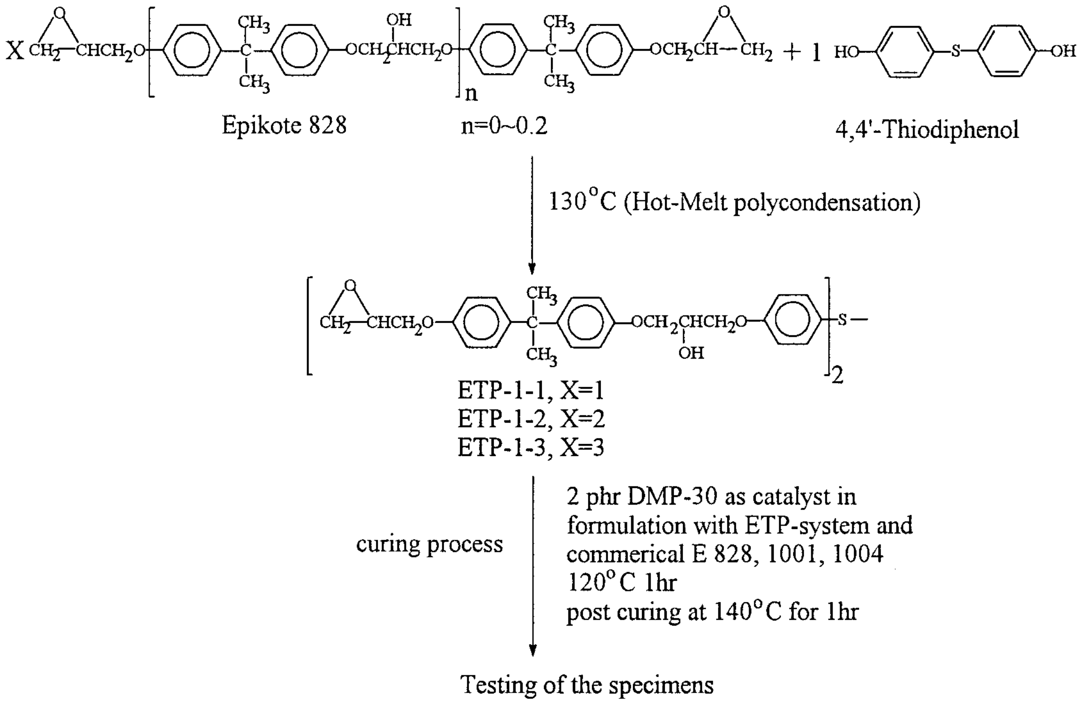
Curing Procedure for TDP-Modified Epoxy Copolymer

The ETP copolymers with 2 phr DMP-30 as the curing agent were mixed at ambient temperature and milled to a fine powder. The resin powder thus obtained was transferred to a mold and cured at 120°C for 1 h and then postcured at 140°C for 1 h.

RESULTS AND DISCUSSIONS

Measurement of Molecular Weight of ETP Epoxy Resin with the Combined Technique of GPC and MALDI–TOF Spectrometer

The essence of the above combination of techniques is to provide true molecular standards from the segment, containing same structural units as the copolymer, for molecular weight determination. The method consists with three parts. The first step is to obtain a global GPC chromatogram of the sample with or without PS as the standards. Next, a series of peaks or the molecular fractionates from GPC's global curves are collected with a semiautomatic fraction collector. Reinjections of a portion of the collected sample is then performed to check the narrower distribution and correct the elution times for these individual fractionates. A spiked method[18] was used in this study for some of the fractionates to reconfirm the exact segment in the global curve and its elution volume, at which the samples were collected. This spiked step is needed as a verification step for the elution time because these fractionates are to be used as standards for determination of the molecular weight and its distribution in the parent sample. The final step of this technique is the use of MALDI–TOF mass spectrometer to determine the molecular weights of the samples either from the reaction aliquots or the fractionates collected from the GPC of the parent sample. With these data, a calibration curve for true molecular weights and distributions is then established.



Scheme 1 Preparation and curing process of ETP copolymers.

Monitoring the Intermediates in the Formation of ETP Epoxy Resins

Preparation of TDP-modified epoxy resin was carried out in hot melt method,[19,20] wherein a 2/1 ratio of E 828/TDP was used for synthesizing the E 828-TDP-E 828 copolymer. Two additional ratios, viz. of 1/1 and 3/1, were also used for the purpose of monitoring the formation of intermediates and their stabilities in different concentration environments. These three copolymers are abbreviated herein after as ETP-1–1, ETP-1–2, and ETP-1–3, with the constant of TDP to the variation of E 828 in molar ratio of 1/1, 1/2, and 1/3, respectively. Scheme 1 shows the preparation of ETP-system copolymers, while the molecular properties of these epoxy and ETP-system copolymers are listed in Table I. It can be seen that the ETP copolymers show a moderate increase in the epoxy equivalent weight (EEW) and exhibit a higher molecular weight (M_w) with a wider molecular weight distribution (MWD) compared to the initial epoxy reactant.

The reaction of TDP and E 828 in ratio 1/2, i.e., that of ETP-1–2, was monitored by GPC. The aliquots were taken at predetermined reaction intervals and subjected to GPC and MALDI–TOF measurements. The results are shown in Figures 1 to 5 for illustrations of the combined technique. GPC chromatograms of the aliquots from the reaction are shown in Figure 1, with their corresponding MALDI–TOF spectra shown in Figure 2. The MALDI–TOF is known to be more sensitive toward low molecular mass than the higher mass. Therefore, the peak intensity can not be used as the quantitation parameter for the determination on the content of the sample. As it can be seen from Figure 2, the mass spectrum from MALDI–TOF is widely spread, and the intensity is not responding to the increases in components of I to III, as they are not well correlated to the change of the content of the same peak in GPC curve. For example, the GPC curves show a diminishing intensity of peak II and the increasing intensity of peak III in Figure 1(c–f) or 1(c–g), while the corresponding mass spectra in Figure 2(c–g) do not alter accordingly. Therefore, the mass data alone does not appear to be adequate to enable the assignment of individual peaks in the GPC global chromatogram to a particular molecular weight.

To obtain the appropriate data, a series of segments was collected with a narrower distribution of molecular weights in GPC chromatogram through a semiautomatic fraction collector. The global and combined individual curves are presented in Figure 3(a,b), with the corresponding

Table I Properties of Modified Epoxy ETP System

	T_g (°C)			TGA wt loss% (°C)[c]		M_w/M_n	
Specimens	Uncured[a]	Cured[b]	EEW (g/mol)	−5%	−10%	GPC[d]	MALDI–TOF[e]
ETP-1-1[f]	45.8	110.8	635–647	376	395	2268/1198	1782/886
ETP-1-2	24.1	102.7	510–520	379	393	1352/918	1138/740
ETP-1-3	7.9	90.5	460–470	374	394	940/718	820/554
E828	16.1	84.2	185–192[g]	325	346	394/392	340/340
E1001[f]	28.0	93.1	450–550[g]	364	386	2030/1086	1742/992
E1004[f]	51.1	94.6	875–1025[g]	369	393	4474/1992	3332/1788

EEW was determined by the HCl/pyridine method for the product after 2 h of reaction.[17]

[a] DSC, heating rate 10°C/min.

[b] After being cured at 120°C for 1 h and 140°C for 1 h.

[c] TGA, heating rate 10°C/min in N_2.

[d] GPC, based on polystyrene standards.

[e] Average, based on MALDI–TOF standards.

[f] M_w calculation with upper limit: ETP-1-1: M_w of 7544 at elution time of 26.2 min. E-1001: M_w of 7522 at elution time of 26.3 min. E-1004: M_w of 8920 at elution time of 24.3 min.

[g] EEW was provided by Shell Chemical Co., locally.

mass spectra of the collected segments shown in Figure 4. The mass data in Figure 4 can now be correlated with the corresponding GPC curves in Figure 3(b). For example, although Figure 4(d) or 4(e) exhibits multiple mass peaks, the peak III or IV in the much simpler mass distributions in these spectra can be related to the corresponding GPC curves of III and IV in Figure 3(b).

As it can be seen from the GPC analysis in Figure 3(b), the sample of fractionate IV is contaminated with segments of III and V (in the bold-lined GPC curve). The corresponding masses of these III, IV, and V segments were determined by MALDI–TOF mass spectrometer, shown in Figure 4(d), and each mass peak correlated well to that in the GPC curve. These data provide us the opportunity to check the elution time and mass data of the fractionates sequentially. The appearance of mass peak III in the spectrum in Figure 4(d) and its disappearance in Figure 4(c) clearly show the usefulness as well as precision of the combined GPC and MALDI–TOF method in combination for measurement of molecular weight.

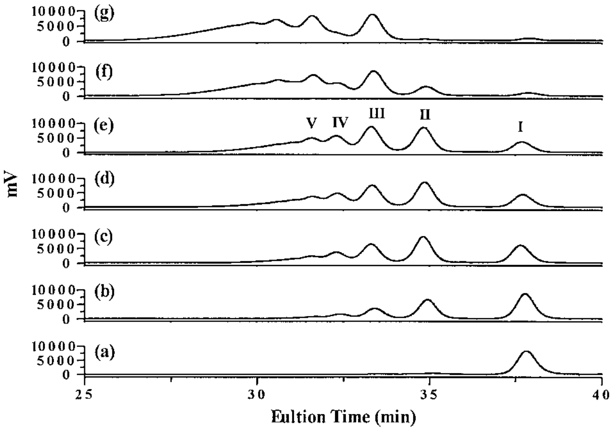


Figure 1 Global GPC chromatograms of the ETP-1–2 reaction intermediates after (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 4 h, and (g) 6 h of reaction.

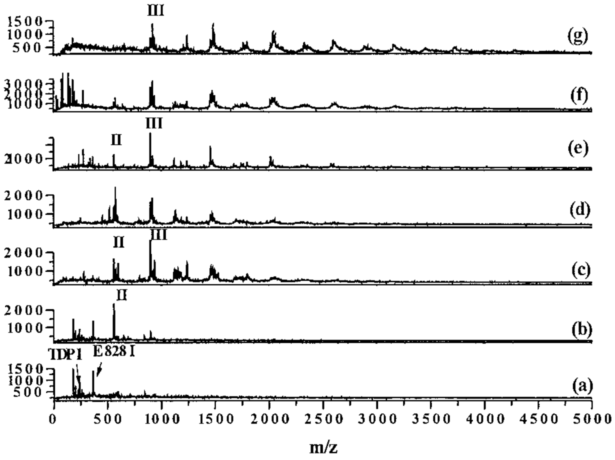


Figure 2 MADLI-TOF mass spectra of the ETP-1–2 reaction after (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 4 h, and (g) 6 h of reaction.

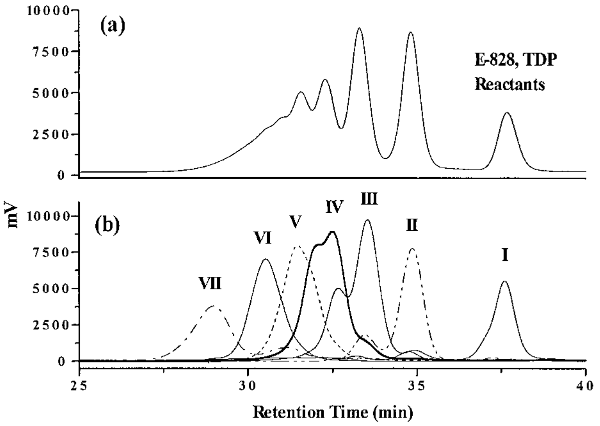


Figure 3 Global and fractionated GPC curves of ETP-1–2: (a) the global curve and (b) the combined curves of the fractionates from ETP-1–2 after 2 h of reaction.

Before using these collected fractionated segments as molecular standards, some selected fractionates were reinjected, as shown in Figure 5, with a spiked method to ensure the correct elution times and as a proper procedure for precise measurement of the data.[18]

The self-standardized calibration curve was then obtained, as plotted in Figure 6, with a PS-standardized curve for comparison. The vast deviations in measured M_w based on the PS standards are shown in Table II. It is clearly illustrated from the calibration curve in Figure 6 that PS-based data cannot be used for structural assignment of the polymeric composition. The deviation in M_w data based on PS standards is 25.5% for low M_w of 602, 25.7% for M_w of 966, and 13.2% for M_w of 1852, just to illustrate.

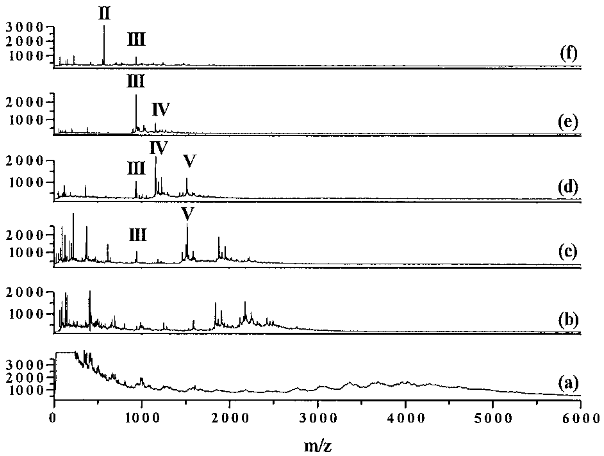


Figure 4 Mass spectra of the collected GPC fractionates (a) curve VII, (b) curve VI, (c) curve V, (d) curve IV, (e) curve III, and (f) curve II of the combined fractionate curves from Figure 3(b).

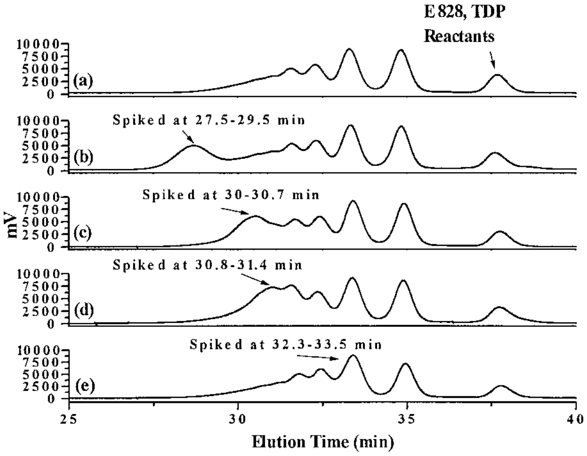


Figure 5 Conformation of the elution times of the fractionates by spiked method. (a) ETP-1–2 epoxy copolymer reacted for 2 h and spiked GPC curves at (b) 27.5–29.5 min, (c) 30–30.7 min, (d) 30.8–31.4 min, and (e) 32.3–33.5 min.

The intermediates in the ETP-1–1 and ETP-1–3 copolymerization reactions can be seen in the

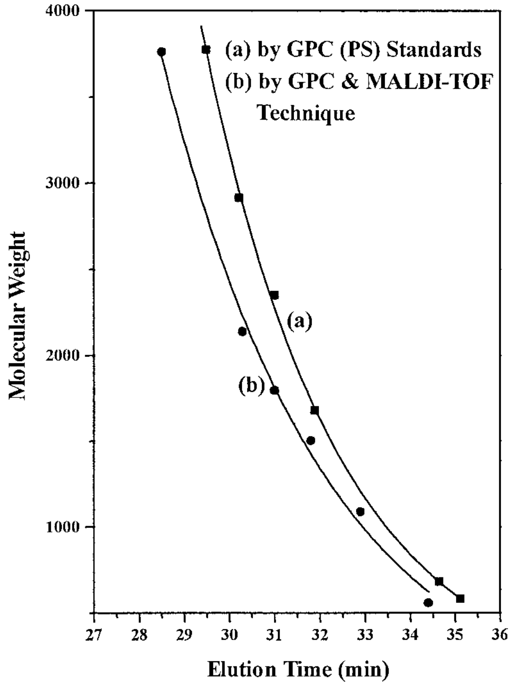


Figure 6 Calibration curve for the TDP-modified epoxy copolymer with fractionates as standards, in comparison to the PS standards: (a) calibration curve by GPC (PS standards) and (b) by combined GPC and MALDI–TOF technique.

Table II Molecular Weight and Distribution of TDP-Modified Epoxy Copolymer, Determined from the Fractionates of GPC Curve

Fractionates	Elution Time Peak (min)	Composition[a] (%)	GPC with PS Standards[b] M_w	M_n	MWD	GPC/MALDI–TOF Method[c] M_w	M_n	MWD	Deviation by PS Standards (%)
TDP and E-828[d]	37.6	9.4	—	—	—	—	—	—	—
(E-828-TDP)$_n$ $n = 1$	34.9	25.5	602	596	1.01	560	556	1.01	7.5
828-(TDP-828)$_n$ $n = 1$	33.2	25.7	966	928	1.04	924	890	1.04	4.5
(TDP-828)$_n$ $n = 2$	32.4	16.2	1426	1362	1.05	1362	1314	1.04	4.7
828-(TDP-828)$_n$ $n = 2$	31.4	13.2	1852	1772	1.05	1730	1672	1.03	7.1
—[e]	30.5	6.1	2412	2322	1.04	2158	2096	1.03	11.8
—[e]	28.8	2.2	5024	4890	1.03	4220	4098	1.03	19.0

Reaction was carried out in hot-melt condition with E-828/TDP ratio of 2 to 1 at 130°C from 2 h.

[a] Based on the peak-fitted area, composition (%) = peak area/total area under the GPC curve.

[b] Average M_w of the peak based on elution time determined with PS standards.

[c] Average M_w of the peak based on mass, measured by MALDI–TOF mass spectrometer.

[d] Both TDP and E-828 appeared at the same elution time. The M_w data on these two compounds were not calculated due to the lack of validity.

[e] Not determined.

GPC chromatograms in Figures 7 and 8, respectively. By comparing the chromatograms of these three copolymers in Figures 1, 7, and 8, it can be noted that the intermediates labeled as peaks I to V are formed in all the reactions, but their contents are vastly different. For ETP-1–1, that is E 828 and TDP in 1/1 ratios (Fig. 7), there are minor peaks of III and IV showing its less content, while for ETP-1–3, i.e., E 828 and TDP in 3/1 ratio (Fig. 8), peak III is found to be the main product. To clearly present the trend of formation, peak II to V, associated with the corresponding intermediates, are individually plotted in Figure 9 for the three different ratios of E 828 to TDP, i.e., copolymers ETP-1–1, ETP-1–2, and ETP-1–3, respectively. The formation of copolymer with these intermediates is summarized in Scheme 2.

From these data, same the following observations can be made: (1) the reaction first proceeds to form 1-to-1 intermediate of E 828-TDP. As can be seen from Figure 9(a), this intermediate forms rapidly and then decreases in concentration to low level after about 6 h. The order of the formation of ETP copolymer is ETP-1–3 > ETP-1–2 >ETP-1–1.

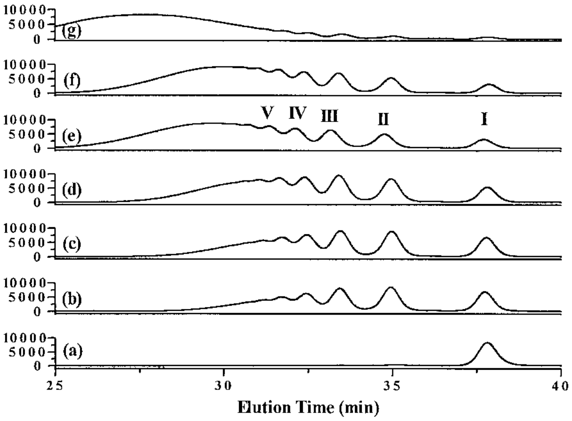


Figure 7 GPC chromatograms of ETP-1–1 reaction intermediates after (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 4 h, and (g) 6 h of reaction.

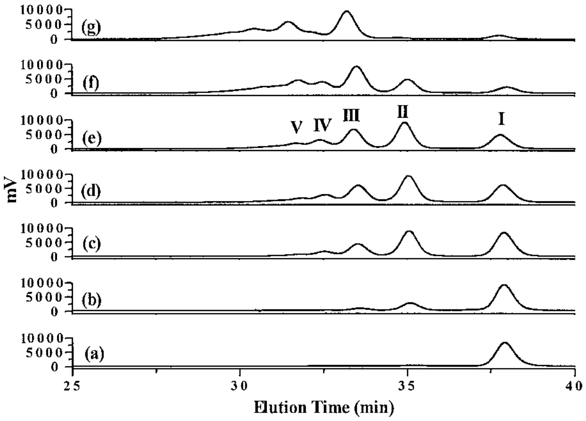


Figure 8 GPC chromatograms of ETP-1–3 reaction intermediates after (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 4 h, and (g) 6 h of reaction.

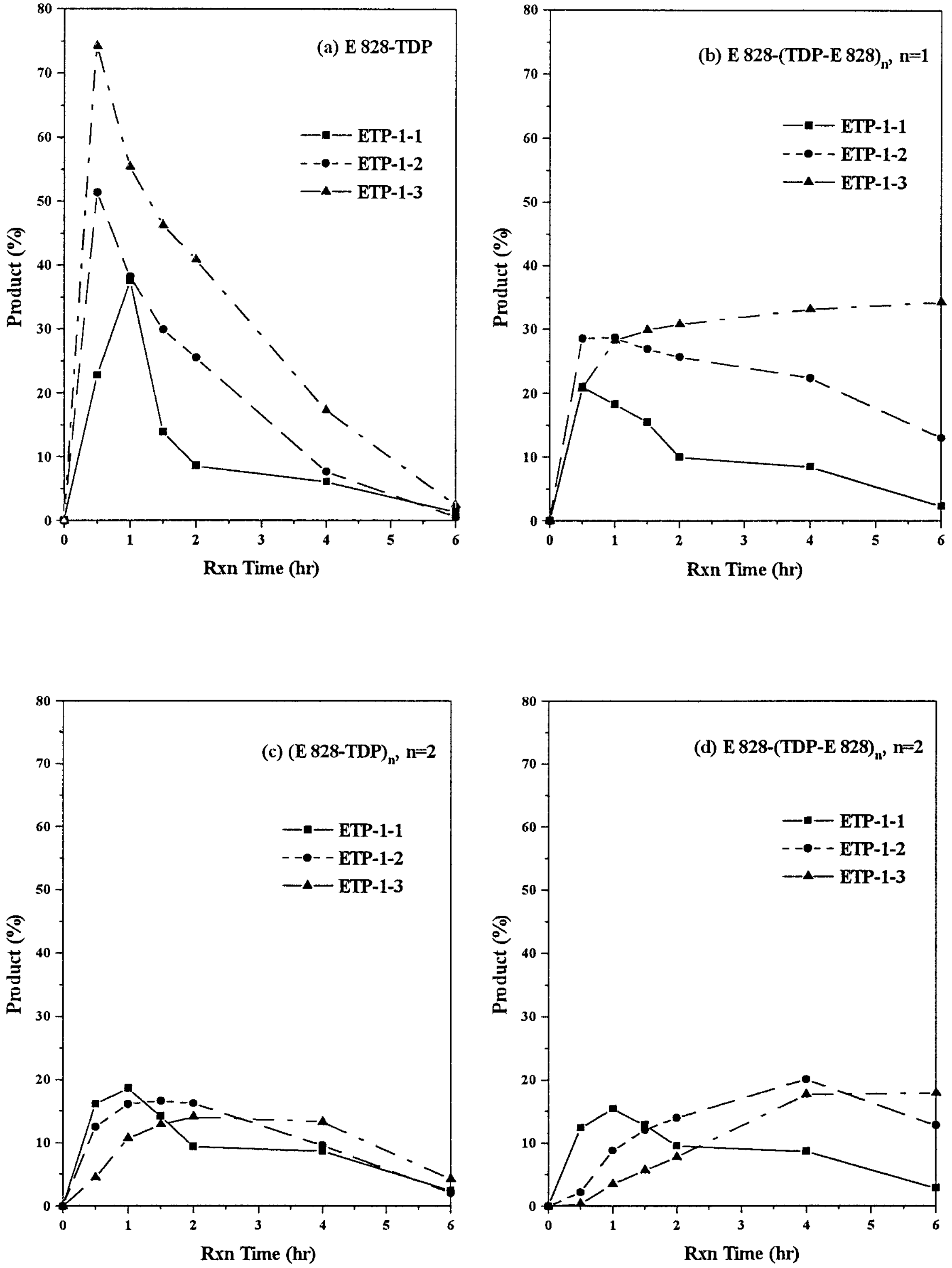
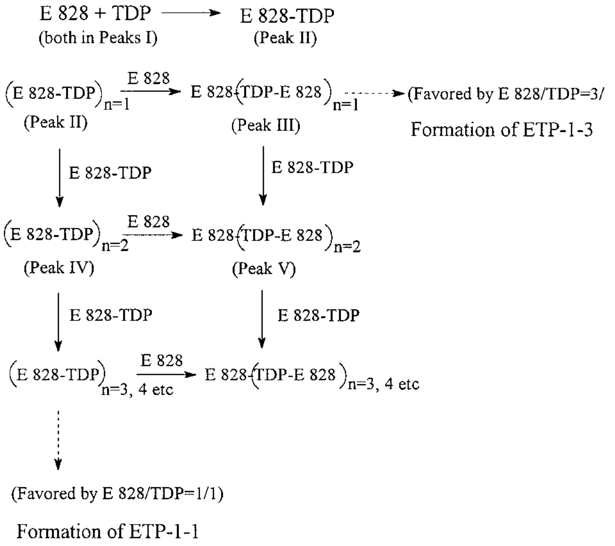


Figure 9 Intermediates in the reaction of E 828 with TDP: (a) E 828-TDP, (b) E 828-(TDP-E 828)$_n$, $n = 1$, (c) (E 828-TDP)$_n$, $n = 2$, and (d) E 828-(TDP-E 828)$_n$, $n = 2$.



Scheme 2 Intermediates in the formation of ETP copolymers.

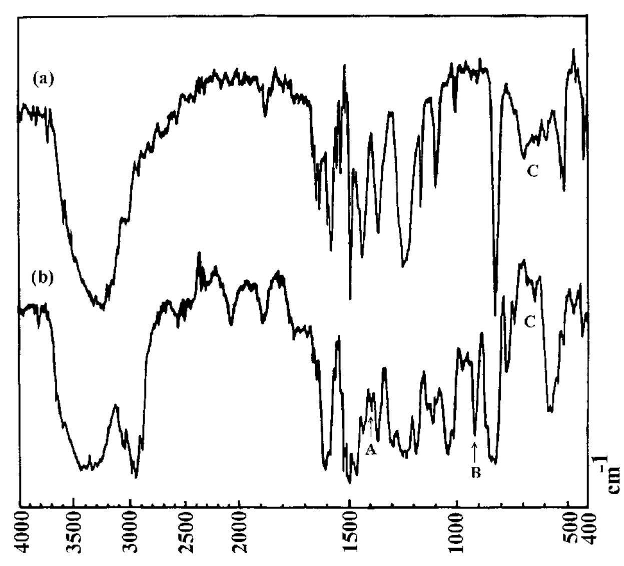


Figure 10 IR spectra of the starting materials and ETP-1–2: (a) TDP, (b) ETP-1–2. The peaks are designated as A: —C(CH_3)$_2$—; B: oxirane; and C: —S—phenyl—.

Apparently, the formation of the intermediates is based on the availability of E 828 in the reaction medium. In the presence of more E 828, the formation of E 828-TDP is undoubtedly faster, as expected. (2) The formation of an ideal E 828-(TDP-E 828)$_n$, n = 1 oligomer, as shown in Figure 9(b), indicates that this oligomer does not form as the main product, unless E 828 is present in excess. The reaction between TDP and E 828 in the ratio 1/2 produced only about 28.6% of this oligomer in 30 min of reaction, and decreased to 13.0% after 6 h. On the other hand, the E 828 to TDP ratio of 3/1 of the content of this n = 1 oligomer reached 34.4% after 6 h of reaction. (3) Higher content of E 828-(TDP-E 828)$_n$, n = 2 oligomer, as shown in Figure 9(d), was also observed for E 828 to TDP ratio of 3/1, at which nearly 17.9% of this n = 2 oligomer was formed. However, after 6 h of reaction, there was little (E 828-TDP)$_n$, n = 1 or 2 remaining in the compositions [Fig. 9(a) and (c)].

The combined contents of E 828-(TDP-E 828)$_n$, n = 1 and n = 2 oligomers constitute 51.3% of the ETP-1–3 copolymer, compared to 25.8% for ETP-1–2 and 5.2% for ETP-1–1. If synthesis of these lower epoxy oligomers is desired, then the best ratio of E 828 to TDP is 3/1.

Structural Determinations of ETP Copolymers

The structure of ETP-1–2, a copolymer with a 4,4′-thiodiphenol, HO—C_6H_4—S—C_6H_4—OH, (TDP) in one-to-two molar ratio with E 828, is presented here as an example of structural determination. The structural identification was based on the IR, ^{1}H-NMR and ^{13}C-NMRs data, as brief by discussed in the following:

The IR spectra of ETP-1–2 and the starting epoxy resin of ETP are shown in Figure 10 for comparison. The IR spectrum of ETP-1–2 in Figure 10(b) exhibits an oxirane peak at 911 cm^{-1} and a weak aryl sulfide absorption at 700–600 cm^{-1}. The oxirane and phenyl groups in ETP-1–2 were observed at their respective positions in the ^{1}H-NMR and ^{13}C-NMR spectra as shown in Figures 11 and 12, respectively. These data confirm the structure of ETP copolymer.

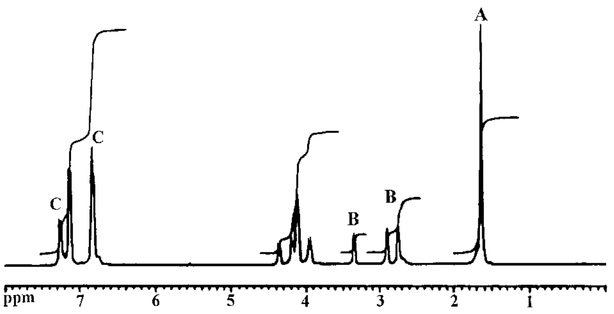


Figure 11 ^{1}H-NMR spectrum of ETP-1–2. The peaks are designated as A: —C(CH_3)$_2$—; B: oxirane; and C: —S—phenyl—.

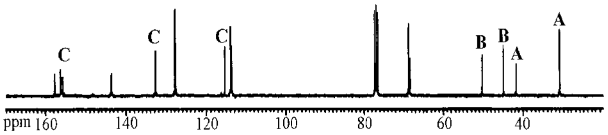


Figure 12 ^{13}C-NMR spectrum of ETP-1–2. The peaks are designated as A: —C(CH$_3$)$_2$—; B: oxirane; and C: —S—phenyl—.

DSC Evaluation of the ETP Epoxy Resins

The composition of ETP-1–3 contains excess of E 828. As can be seen from Figure 8(g), E 828 is still detectable as peak I. The use of E 828 as an active liquid thinner is rather common in epoxy formulation. Because it contents less aromatic segments of BPA in its content than E-1000 series, the E 828 has been known[21] to possess the lower T_g than its higher homologs. Therefore, the effect of E 828 in ETP copolymers was evaluated by DSC, and the corresponding thermograms of the curing process before and after the addition of curative DMP-30 and cured at 120°C are shown in Figures 13 and 14, respectively. From these DSC data, the order of variation in T_g is noted as follows: for uncured resins, the order of T_g is: E 1004 > ETP-1–1 > E 1001 > ETP-1–2 > ETP-1–3 > E 828, in decreasing order.

For cured resins, the order of T_g is: ETP-1–1 > ETP-1–2 > E 1004 > E 1001 > ETP-1–3 > E 828, in decreasing order.

From these orders of variations in T_g, it can be noted that the presence of E 828 in ETP-1–3 copolymer indeed shows a lowering of T_g, as indicated by the order: ETP-1–1 > ETP-1–2 > ETP-1–3. However, all these copolymers still exhibit higher T_g than E 828.

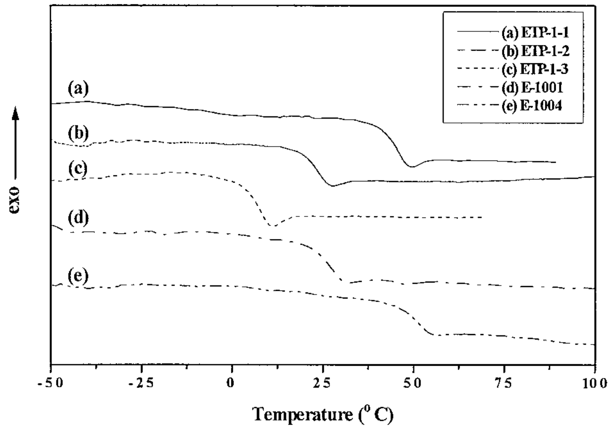


Figure 13 The T_gs of the epoxy resins: (a) ETP-1–1, T_g = 45.8°C, (b) ETP-1–2, T_g = 24.1°C, (c) ETP-1–3, T_g = 7.9°C, (d) E 1001, T_g = 28.0°C, and (e) E 1004, T_g = 51.1°C.

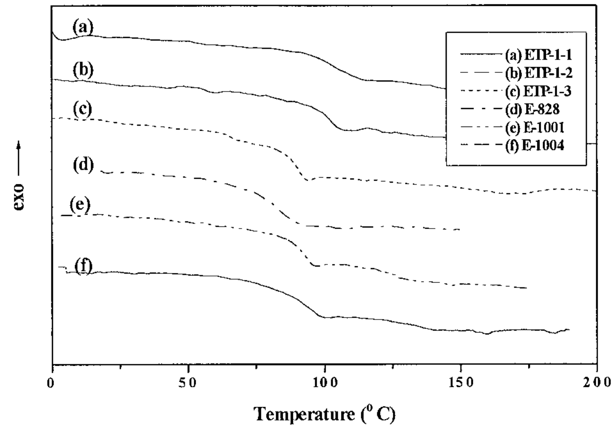


Figure 14 The T_gs of the epoxy resins cured with DMP-30 1 h at 120°C and 1 h at 140°C: (a) ETP-1–1, T_g = 110.8°C, (b) ETP-1–2, T_g = 102.7°C, (c) ETP-1–3, T_g = 90.5°C, (d) E 828, T_g = 84.2°C, (e) E 1001, T_g = 93.1°C, and (f) E 1004, T_g = 94.6°C.

TGA Analysis of ETP Copolymers and Epikote Resins

ETP copolymers were subjected to TGA evaluation for determining their thermal stability. The TGA thermograms were combined and are shown in Figure 15 for ETP copolymers and Epikote resins. The ETP copolymers, as listed in Table I, exhibited the rival stability comparable to that of E 1001 and E 1004. As an example, the temperature at 5% weight loss, in decreasing order, was found to be 379°C for ETP-1–2; 376°C for ETP-1–1; 374°C for ETP-1–3; 369°C for E 1004; 364°C for E 1001; and 325°C for E 828.

CONCLUSION

A method of monitoring the formation of copolymers is described here. The reaction intermediates, as monitored by true molecular weights by using a combination of GPC and MALDI–TOF methods, indicated that the optimum ratio of E 828 to TDP for formation of the ideal oligomer of E 828-(TDP-E 828)$_n$, n = 1 is 3/1, at which, the amount of this oligomer is 34.4%, while that of n = 2 is 17.9, with less than 2.5% of (E 828-TDP)$_n$, n = 1.

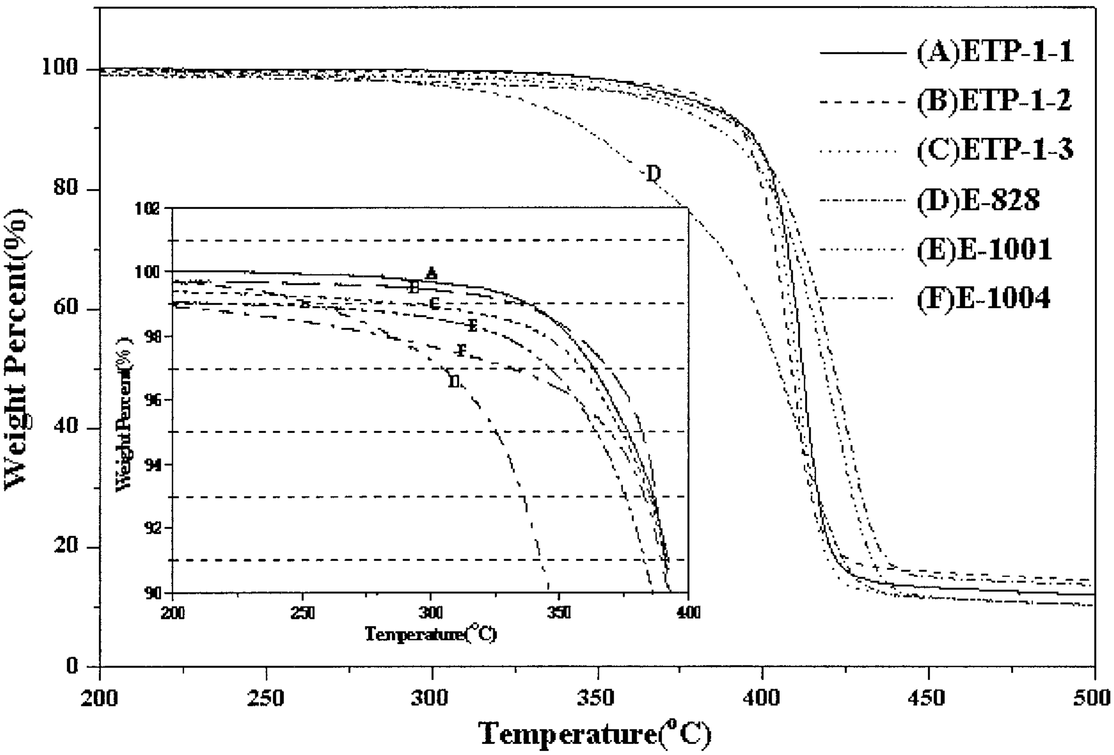


Figure 15 TGA thermograms of ETP epoxy copolymers and DGEBA resins.

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