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# Determination of residual levels of unsaturation in partially hydrogenated poly(2,3-diphenyl-1,3-butadiene) using thermogravimetry

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## Abstract

The thermal degradation characteristics of head-to-head poly(styrene) (HHPS) should provide insight with respect to the impact of head-to-head placement on the thermal stability of the traditional atactic head-to-tail polymer (HTPS). The synthesis of head-to-head poly(styrene) must be accomplished indirectly. The HHPS is most satisfactorily obtained by dissolving metal reduction of poly(2,3-diphenyl-1,3-butadiene) (PDBD) generated by radical polymerization of the corresponding diene monomer. Full saturation of the polymer mainchain requires several iterations of the reduction procedure. Since the decomposition of PDBD is prominent at 374 °C and that for HHPS is similarly facile at 406 °C, it seemed feasible that TGA of partially hydrogenated PDBD might be utilized as a convenient means of monitoring the extent of hydrogenation. This has been demonstrated for various levels of unsaturation remaining—from approximately 90 to less than 10%. Within this range the peak areas from the DTG plots of the partially hydrogenated polymer provide a good reflection of the ratio of unsaturated to saturated units in the polymer. Even low levels of unsaturation in the polymer may be detected by the asymmetry of the decomposition peak for the polymer.

*Keywords:* Head-to-head poly(styrene); Polymer composition by TG; Polymer modification

## 1. Introduction

The thermal degradation of poly(styrene) has long been known and has limited the processing window for the polymer [1]. This is particularly true for material to be used in food packaging. The presence of even very low levels of monomer generated by polymer degradation during formation of an item of packaging can have a significant negative impact on the taste and aroma of contained food. Although, the degradation has been variously studied it is not yet well understood [1–16]. A notion that has persisted is that degradation is initiated at head-to-head linkages present in the polymer as a consequence of polymerization termination by radical coupling. The availability of a polymer with only head-to-head links would permit a direct examination of the thermal lability of this structure. Head-to-head poly(styrene) (HHPS) must be prepared indirectly. Most commonly, it is obtained by the hydrogenation of poly(2,3-diphenyl-1,3-butadiene) (PDBD). For this process it is essential that a rapid, convenient method for monitoring the extent of hydrogenation be available. Since the thermal properties of the precursor polymer and HHPS are

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quite different it was felt that thermogravimetry might provide such a method.

## 2. Experimental

### 2.1. Methods and instrumentation

Monomers and polymers were characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra ($^1$H and $^{13}$C) were obtained in deuterochloroform using a General Electric QE-300 spectrometer. Infrared spectra were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs using a model 560 Nicolet MAGN-IR spectrophotometer. Ultraviolet spectra of the polymers were obtained using dilute solutions in THF and a CARY 1 UV-Vis spectrophotometer. The scanned wavelength ranged from 200 to 400 nm. Molecular weights or the polymers were routinely determined by size exclusion chromatography (SEC) using solutions in THF, miscrostyrogel columns, and linear poly(styrene) calibration. For branching studies, solutions were prepared at a concentration of 1 ml/min in THF and filtered through a 0.2 μm PTFE filter. The injection volume was 50 μl. THF was used as eluant at 1 m/min. Separation was accomplished with three mixed bed columns (Polymer Laboratories) in series. For detection a Viscotek model H-502 differential viscometer was used in series with a Waters 2410 differential refractive index detector. Columns and detectors were held at 35 °C. Narrow distribution poly(styrene) standards were used to generate the universal calibration curve. Polystyrene 1683, a broad, linear poly(styrene) standard was used to verify system performance. The glass transition temperatures ($T_g$) of polymers were determined using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min, using a TA Instruments Inc. Thermal Analyst model 2100 system equipped with a model 2910 MDSC cell. The sample compartment was subject to a constant purge of dry nitrogen at 50 ml/min. The thermal degradation characteristics of PDBD and HHPS were examined by thermogravimetry using a TA instruments model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TGA cell was swept with nitrogen at 50 ml/min during degradation runs. The sample size was approximately 5–10 mg in a platinum sample pan. The temperature was ramped at a rate of 2° or 10 °C/min.

### 2.2. Materials

*2,3-Diphenyl-2,3-butanediol*. A medium pressure mercury arc lamp, a thermometer and a condenser were fitted to a 500 ml, three-necked photoreaction flask. A mixture of 51.0 g (0.43 mol) of acetophenone and 400 ml of freshly distilled 2-propanol was placed in the flask. The reaction vessel was purged with dry nitrogen overnight. One drop of glacial acid was added to the mixture and irradiation was initiated. After irradiation with water cooling for 8 h, a yellow-colored solution was obtained. The solvent was removed from the solution by rotary evaporation at reduced pressure (20 Torr) to provide an oily residue which was allowed to stand. The 2,3-diphenyl-2,3-butanediol crystallized slowly and was isolated by filtration on a fritted glass funnel and washed with 200 ml of a mixture of acetone–petroleum ether (b.p. 35–50 °C) (1:4); the yield was 35 g (70%) of colorless needles, m.p. 124.9 °C (DSC) after two recrystallizations from acetone–petroleum ether. The $^1$H NMR spectrum of this material consists of a singlet $\delta$ db 1.49 (6 H, methyl protons), a board singlet at $\delta$ 2.61 (2 H, hydroxyl protons) and a multiplet at $\delta$ 7.23 (10 H, aromatic protons). The $^{13}$C spectrum contains absorptions at 24.9 (methyl C), 78.8 (C adjacent to oxygen), 127.0, 127.1, 127.3 (phenyl $C_2$, $C_3$, $C_4$) and 143.4 (phenyl $C_1$). The mass spectrum contains a base peak at *m/e* 121 ($Ph(CH_3)C+$ (OH)).

*2,3-Diphenyl-1,3-butadiene*. Into a 250 ml, three-necked, round-bottomed flask equipped with a Liebig condenser bearing a gas-inlet tube, a magnetic stirring bar and a thermometer was placed 4.84 g (0.020 mol) of 2,3-diphenyl-2,3-butanediol and 0.08 g (0.65 mmol) of 4-(dimethylamino)pyridine (DMAP) dissolved in 100 ml of dry pyridine. The solution was brought to solvent reflux and 2.0 ml (0.021 mol) of phosphoryl chloride was added. The mixture was stirred at solvent reflux for 108 h. The mixture was allowed to cool to near room temperature and 15% aqueous hydrochloric acid solution was added until the pH of the mixture was 6.0. The mixture was extracted with three 50-ml portions of diethyl ether. The ether extracts were combined and washed with two 50-ml portions of saturated aqueous sodium chloride solution. The ether solution was dried over an anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure to afford an oily residue which was allowed to stand. The product, 2,3-diphenyl-1,3-butadiene, slowly crystallized from the oil. The crystals, 2.4 g (58.2%), were collected by filtration at reduced pressure and purified by column chromatography using silica gel (60–100 mesh) with hexane-ethyl acetate (10:1) as eluant. The purification was monitored by periodic analysis of the column eluant by TLC. The eluant was divided into 10 portions of 50 ml each. Fractions 4–8 were combined and the solvent was removed by rotary evaporation at reduced pressure. The residue was recrystallized from methanol to provide pure 2,3-diphenyl-1,3-butadiene (1.9l g; 79.6% of the crude product) as colorless needles m.p. 48.4 °C (DSC). The $^{1}$H NMR spectrum of this compound contains absorptions at $\delta$ 5.30 (d, 2 H) and $\delta$ 5.54 (d, 2 H), terminal methylene protons, and $\delta$ 7.25 and $\delta$ 7.38 (m, 10 H), aromatic protons. The $^{13}$C NMR spectrum contains absorptions at $\delta$ 116.4, 127.5, 128.1, 140.1 and 149.8. The mass spectrum of this compound contains a base peak at *m*/*e* 206.

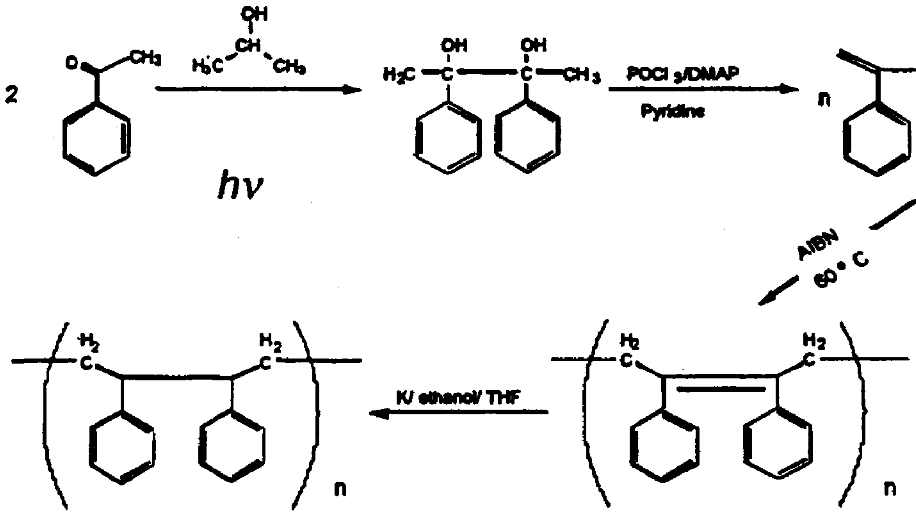
*PDBD*. 2,3-Diphenyl-1,3-butadiene was polymerized in a sealed polymerization tube using freshly crystallized AIBN as initiator in benzene solution (8.04 mmol/l). A 50-ml polymerization tube with a two-way stopcock was charged with AIBN solution (4 ml, 0.032 mmol of AIBN) and 4.8 g (23.3 mmol) of 2,3-diphenyl-1,3-butadiene. The polymerization tube was warmed at 55 °C to afford a homogeneous solution which was degassed at 3 Torr using the freeze-thaw technique (five repetitions), and sealed under nitrogen. The polymerization was carried out by placing the tube in a constant temperature bath at 60 °C. After 86 h, the tube was opened and the solid polymer was dissolved in 200 ml of benzene. The solution was added dropwise into 2000 ml of methanol to precipitate the polymer. The polymer was collected by filtration and dried at 40 °C (0.1 Torr) overnight. The $^{1}$H NMR spectrum of the polymer contains absorptions at $\delta$ 2.06 (4 H, methylene protons) and $\delta$ 6.89 (10 H, aromatic protons). This spectrum contains no absorption in the olefinic region indicating that the polymer did not contain pendant vinyl groups, i.e. the polymerization occurred in 1,4-fashion. The $^{13}$C NMR spectrum contains sets of absorptions corresponding to the polymer of *cis* and *trans* configuration at the double bond of the mainchain at 34.2 and 32.4, 126.0 and 125.4, 128.3 and 127.2, 129.8 and 129.6, 137.0 and 137.5, and 142.6 and 141.9. The ratio of *cis* to *trans* absorptions by electronic integration is 53:47. This is very close to 1:1 and suggests that there is no great preference for one stereoisomeric arrangement over the other. The UV spectrum (THF) contains maximum absorption at 252 nm ($\varepsilon_{\max} = 4.3 \times 10^{3}$ l/mol cm). Dual detection SEC analysis indicated that the polymer was unbranched with $M_{\mathrm{W}} = 1.6 \times 10^{5}$, $M_{\mathrm{n}} = 5.3 \times 10^{5}$ and $M_{\mathrm{W}}/M_{\mathrm{n}} = 3.03$.

*HHPS*. Into a dry, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser bearing a gas-inlet tube and a three-way stopcock was placed PDBD, 1.0 g (4.9 mmol), under a flow of dry nitrogen. Dry THF (100 ml) and dry ethanol (5.7 ml, 98 mmol) were added through the three-way stopcock by means of a hypodermic syringe. Potassium metal 3.7 g (0.095 g atom) was added portionwise as the reaction mixture was stirred magnetically under dry nitrogen. The solution became cloudy as potassium ethoxide formed. After 24 h, the reaction was stopped by adding 20 ml of ethanol to destroy excess potassium. The solution was dropped into 600 ml of methanol to precipitate the polymer, which was collected by filtration and dried at 25 °C and 20 Torr overnight. The recovery was 0.92 g (92%). The degree of hydrogenation was 84% as determined using UV spectroscopy. The hydrogenation procedure was repeated twice to obtain the completely hydrogenated product, HHPS. The polymer was repeatedly (4×) dissolved in toluene and precipitated by the addition of methanol to remove any residue from the reduction and then dried at 40 °C and 0.1 Torr for 24 h. The glass transition temperature, $T_{\mathrm{g}}$, for the polymer determined by DSC was 104 °C. Analysis by SEC indicated that it was an unbranched polymer with $M_{\mathrm{W}} = 1.4 \times 10^{5}$, $M_{\mathrm{n}} = 4.9 \times 10^{4}$ and $M_{\mathrm{W}}/M_{\mathrm{n}} = 2.86$. The proton NMR spectrum of the polymer contains absorptions at $\delta$ 0.95 (2 H, methylene protons), $\delta$ 2.11 (1 H, methine proton) and $\delta$ 6.85 (5 H, aromatic protons). The $^{13}$C NMR spectrum contains a multiplicity of absorptions due to the presence of polymer of both *erythro* and *threo* configuration. The chemical shifts are 31.0, 51.0, 126.1, and 125.4, 127.2 and 127.1, 129.0 and 128.7, and 143.9 and

142.8. The UV spectrum (THF) contains a maximum absorption at 252 nm with $\varepsilon_{\max} = 67$ l/mol cm.

## 3. Results and discussion

Head-to-head linkages in conventional atactic poly(styrene) are thought too be weak links at which thermal degradation can be initiated [5,6,15]. To examine the lability of this structure it was necessary to prepare the fully head-to-head polymer. This can be done by hydrogenation of PDBD [15]. The overall synthesis of this precursor polymer based on inexpensive acetophenone as starting material is shown in Scheme 1. Photoreduction of acetophenone provided 2,3-diphenyl-2,3-butanediol. Dehydration of the diol using an equimolar amount of phosphoryl chloride in pyridine containing a catalytic amount of DMAP at 90–100 °C produced the monomer, 2,3-diphenyl-1,3-butadiene. Polymerization of the monomer in benzene solution at 60 °C using AIBN as initiator produced PDBD. Several observations suggest that the monomer had undergone 1,4-polymerization. The infrared spectrum of the polymer (see Fig. 1) contains no absorption for the terminal olefinic methylene group that would have been formed if 1,2-polymerization had occurred to a substantial extent. The proton NMR spectrum of the polymer is displayed in Fig. 2. The spectrum contains a peak for the phenyl group at $\delta$ 6.89 and a peak for the methylene protons at $\delta$ 2.06. The spectrum does not contain absorption for terminal methylene protons. At the sensitivity of proton NMR (which was done at room temperature using a 300 MHz instrument) no ethylene protons indicative of vinyl end groups could be detected. The carbon-13 NMR spectrum of the polymer contains peaks at $\delta$ 142.61 and $\delta$ 141.90 which may be assigned to C1 of the phenyl group which is attached *cis* and *trans* to the olefinic carbon atoms. The chemical shifts of the olefinic carbon atoms are $\delta$ 137.91 and $\delta$ 137.54 for the *cis*-carbon atom and *trans*-carbon atom, respectively. These two peaks disappear from the spectrum upon hydrogenation of the polymer. The chemical shifts of the methylene carbon atoms attached *cis* and *trans* to an olefinic linkage are $\delta$ 34.16 and $\delta$ 32.34, respectively. The ratio of the peak areas by electronic integration for the *cis* and *trans* absorptions is 53:47. This is very close to 1:1 and suggests that there is no great preference for one stereoisomeric arrangement over the other. The details of the chemical shift data are listed in Table 1. The multiplicity of chemical shifts may be attributed to the *cis* and *trans* configurations about the double bonds of the polymer mainchain. In addition to the spectroscopic evidence, careful examination of the polymer by SEC provided no indication



Scheme 1. Synthesis route to HHPS.

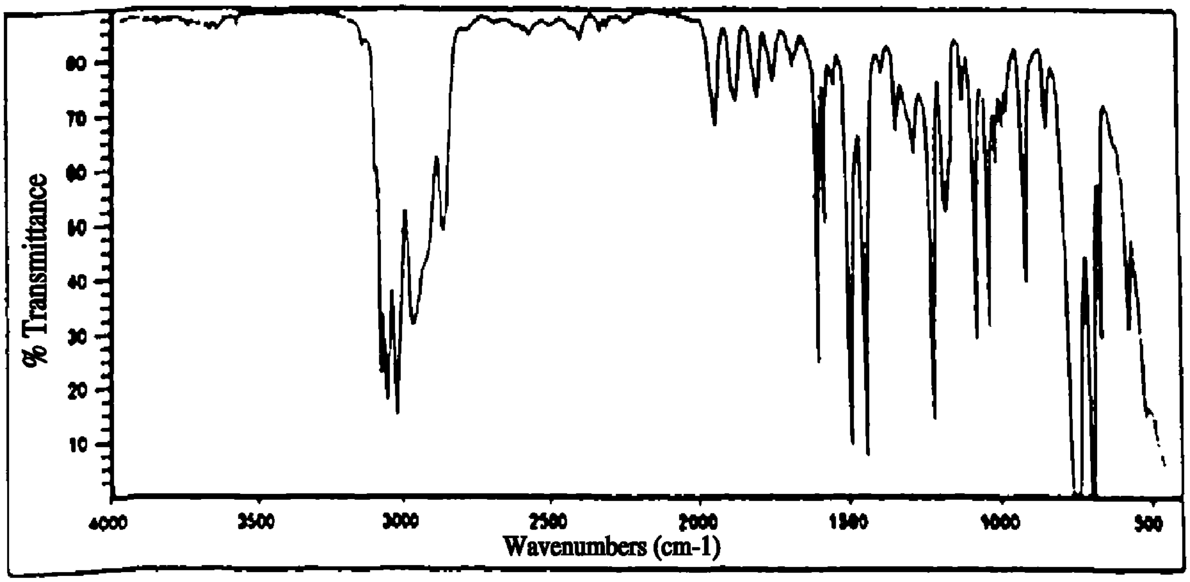


Fig. 1. Infrared spectrum of PDBD produced by radical polymerization in benzene at 60 °C.

of branching. HHPS was obtained by hydrogenation of PDBD with potassium and ethanol in dry THF as solvent. The reduction process had to be repeated two or three times to achieve full reduction (see Fig. 3).

The progress of the hydrogenation of PDBD was determined by ultraviolet spectroscopy at 252 nm. With progress of the reduction of the 2,3-double bonds of PDBD, the absorption at 252 nm decreased. At 252 nm, the molar absorptivity of PDBD was

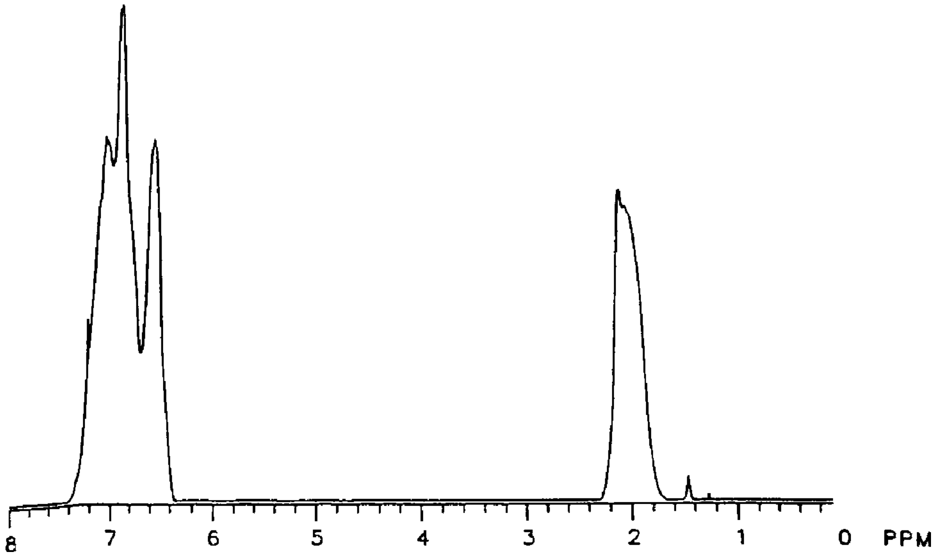
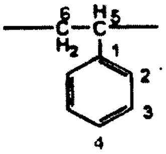


Fig. 2. Proton NMR spectrum of PDBD produced by radical polymerization in benzene at 60 °C.

Table 1
Chemical shifts in the $^{13}$C NMR spectrum of PDBD

| Carbon atom[a] | Chemical shift ($\delta$)[b] | |
|---|---|---|
| | *cis* | *trans* |
| C1 | 142.61 | 141.90 |
| C2 | 129.76 | 129.59 |
| C3 | 128.26 | 127.16 |
| C4 | 126.05 | 125.36 |
| C5 | 137.91 | 137.54 |
| C6 | 34.16 | 32.37 |

[a] Carbon atom numbering as follows:



[b] Relative to TMS.

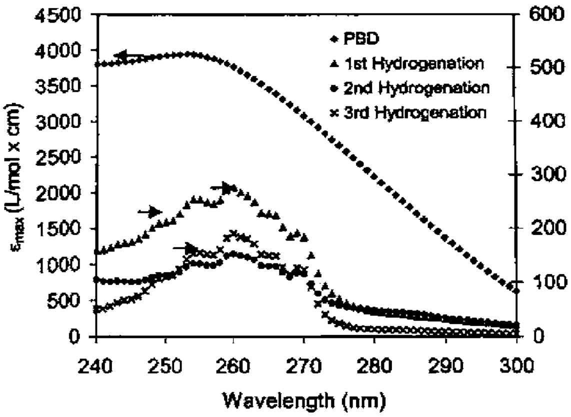


Fig. 3. Ultraviolet spectra of PDBD, partially hydrogenated PDBD and HHPS.

Table 2
Glass transition temperatures for PDBD, partially reduced PDBD, HHPS and atactic head-to-tail poly(styrene)

| Polymer | Glass transition temperature, $T_g$ (°C) |
|---|---|
| PDBD[a] | 120.5 |
| 68.3% hydrogenated PDBD[b] | 100.2 |
| 94.9% hydrogenated PDBD[b] | 104.2 |
| HHPS | 104.3 |
| Atactic head-to-tail poly(styrene) | 107.6 |

[a] Poly(2,3-diphenyl-1,3-butadiene).

[b] Determined from the ratio of molar absorptivity for PDBD.

$4.3 \times 10^3$ l/cm mol and that of HHPS was 67 l/cm mol, different by a factor of 67. Thus the conversion of PDBD to HHPS could readily by monitored using ultraviolet spectroscopy.

The glass transition temperatures for the two polymers were determined by DSC and are displayed in Table 2. The thermal degradation by characteristics of PDBD partially hydrogenated PDBD, HHPS, and atactic head-to-tail poly(styrene) were examined by TGA. Onset temperatures and the temperatures for maximum degradation rate are listed in Table 3.

A sample of partially reduced PDBD with significant unsaturation remaining (about 32%) when subjected to thermogravimetry displayed two major weight losses. The corresponding temperatures of maximum degradation rate are at 376 and 400 °C, respectively. The former corresponds to the temperature of maximum degradation rate for PDBD. The first weight loss peak began to disappear from the thermogram when the level of hydrogenation reached

Table 3
Thermal degradation of PDBD, partially reduced PDBD, HHPS and tactic head-to-tail poly(styrene)

| Polymer | Onset temperature for degradation (°C)[a] | Temperature of maximum degradation rate (°C)[b] |
|---|---|---|
| PDBD[c] | 323 | 374 |
| 68.3% hydrogenated PDBD[d] | 322 | 376/400 |
| 94.9% hydrogenated PDBD[d] | 364 | 402 |
| HHPS | 370 | 406 |
| Atactic head-to-tail poly(styrene) | 363 | 409 |

[a] Extrapolated onset temperature from the derivative plot of weight loss versus temperature.

[b] Maximum in the derivative plot of weight loss versus temperature.

[c] Poly(2,3-diphenyl-1,3-butadiene).

[d] Determined from the ratio of molar absorptivity for PDBD and HHPS.

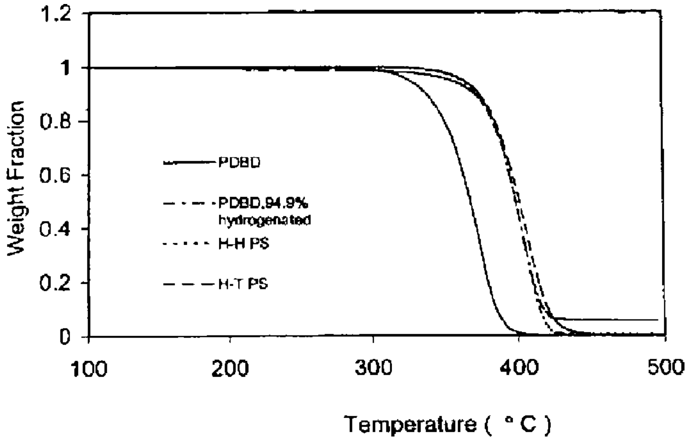


Fig. 4. TGA plots for PDBD, partially hydrogenated PDBD, HHPS and atactic head-to-tail poly(styrene).

90% (10% 2,3-double bond left in the polymer chain). The extrapolated onset temperature for the degradation and temperature of maximum degradation rate increased to 364 and 402 °C, respectively. The thermal decomposition data and TGA plots for PDBD at different levels of hydrogenation are listed in Table 3 and Fig. 4, respectively.

Clearly, the thermal decomposition behavior of partially hydrogenated PDBD is dependent on the level of unsaturation remaining in the sample. To determine whether or not TGA might be used as a convenient means to monitor the extent of hydrogenation of PDBD the thermal degradation behaviors of mixtures of different ratios of PDBD and HHPS were determined by TGA. It is readily appears that

1. the plots for mixtures of PDBD and HHPS are very similar to those of partially hydrogenated PDBD containing an equivalent level of unsaturation, and
2. with as little as 10% PDBD in the mixture the peak reflecting the unsaturated polymer is still clearly evident.

As may be seen in Fig. 5, when low levels of unsaturation are present in the polymer the level is hard to determine quantitatively because of the overlap of the peaks corresponding to the unsaturated and

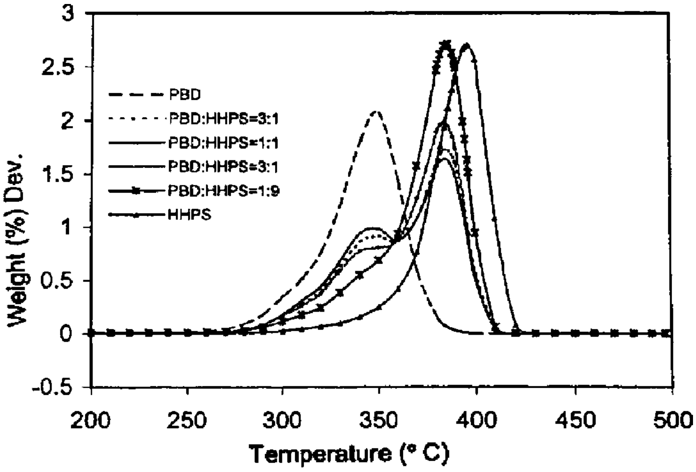


Fig. 5. DTG Plots for mixtures of PDBD and HHPS.

saturated polymers, respectively. Nonetheless, the presence of even low levels of unsaturation may be detected by the asymmetry of the decomposition peak for the polymer. Therefore, TGA can readily provide a useful reflection of the level of reduction of partially hydrogenated samples of PDBD.

## 4. Conclusions

Thermogravimetry provides a useful and convenient method for the determination of the residual level of unsaturation in partially hydrogenated PDBD. This permits the ready monitoring of the conversion of PDBD to the corresponding saturated polymer, HHPS.

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