

# Synthesis, Structure, and Properties of Poly(styrene-co-pentabromobenzyl acrylate) Materials

Y. YUAN,<sup>1,\*</sup> A. SIEGMANN,<sup>1</sup> and M. NARKIS<sup>2,†</sup>

<sup>1</sup>Department of Materials Engineering and <sup>2</sup>Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, 32000, Israel

## SYNOPSIS

Polymers and copolymers of pentabromobenzyl acrylate (PBBA) with styrene were synthesized and characterized. Poly(PBBA) exhibits a rather high glass transition temperature ( $T_g$ ) and good solvent resistance. The incorporation of PBBA moiety into polystyrene (PSt) enhances  $T_g$ , improves the thermal stability, and also does not adversely affect polystyrene's mechanical properties. Copolymers prepared through both emulsion semibatch and batch processes exhibit random chain structures and possess similar properties such as  $T_g$ , inherent viscosity, and mechanical properties. Blends of poly(PBBA) and PSt demonstrate immiscible phase behavior, however their thermal stabilities are similar to the copolymers' stability at the same PBBA content. It is thus shown that the thermal stability of the systems investigated in this work is essentially affected by composition, regardless of the distribution and dispersion of the PBBA polymer or copolymers. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymers containing bromine above a certain level are known to exhibit flame retardancy.<sup>1,2</sup> Pentabromobenzyl acrylate (PBBA),  $T_m = 121^\circ\text{C}$ , has a bromine content of 71 wt %, and both the monomer and polymer have been used as flame retardants. For instance, PBBA can be used as a reactive additive for engineering thermoplastics,<sup>3</sup> thus poly(PBBA) was blended with commercial polyester to enhance properties such as flame retardance and heat resistance, and to improve processability.<sup>4</sup> Pyrolysis of poly(PBBA)/nylon 6,6 blends was studied at  $1400^\circ\text{C}$ , revealing that  $\text{CH}_3\text{CH}_2\text{Br}$  was generated and acted as a volatile flame retardant for the nylon in the vapor phase.<sup>5,6</sup>

The synthesis and properties of PBBA polymer and copolymers with other vinyl monomers have not yet been reported in the literature. Bulk polymerization of PBBA above its melting point ( $120-$

$290^\circ\text{C}$ ) was described in a patent.<sup>7</sup> In the present work, poly(PBBA) was synthesized by solution polymerization in toluene, and copolymers with styrene were synthesized through emulsion semibatch and batch copolymerization procedures. The aim of this work is to study the effects of PBBA content and the emulsion polymerization process on the copolymers' structure-property relationships.

## EXPERIMENTAL

### Materials

PBBA was supplied by Bromine Compounds Ltd., Israel and used as received. The differential scanning calorimetry (DSC) melting point is  $120^\circ\text{C}$ . Styrene was twice washed with 5% NaOH aqueous solution before use. Sodium lauryl sulphate (Merck), Triton X-180 (Bio-Lab, Israel),  $\text{K}_2\text{S}_2\text{O}_8$  (Merck),  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  (Merck), toluene (Bio-Lab), and bromobenzene (Fluka) were used as received. Polystyrene (PSt) for solution blending with poly(PBBA) was supplied by Carmel Olefins, Israel as a general purpose clear PSt.

\* Permanent address: Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China.

† To whom correspondence should be addressed.

**Table I Emulsion Copolymerization Formulation at 70°C<sup>a</sup>**

| Ingredients                                                      | Batch Process<br>in Reactor | Semibatch Process |          |          |
|------------------------------------------------------------------|-----------------------------|-------------------|----------|----------|
|                                                                  |                             | In Reactor        | Funnel 1 | Funnel 2 |
| Monomers <sup>b</sup>                                            | 47.0 g                      |                   |          | 47.0 g   |
| 1% SLS <sup>c</sup>                                              | 30 mL                       | 20 mL             | 10 mL    |          |
| Triton X-100 (18%)                                               | 25 mL                       | 15 mL             | 10 mL    |          |
| DD-water <sup>d</sup>                                            | 80 mL                       | 55 mL             | 25 mL    |          |
| 3% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>                  | 5 mL                        |                   | 5 mL     |          |
| Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> 10H <sub>2</sub> O | 0.05 g                      | 0.05 g            |          |          |

<sup>a</sup> Solid content is 25 wt %.

<sup>b</sup> Maximum PBBA content is 70 wt %.

<sup>c</sup> Sodium lauryl sulphate.

<sup>d</sup> Distilled and deionized water.

### Poly(PBBA) Synthesis

A solution of 5.0 g PBBA in 25 mL toluene was flushed by N<sub>2</sub> for 30 min and then heated to 80°C under N<sub>2</sub> atmosphere. Upon the addition of 0.07 g benzoyl peroxide (BPO) initiator, the reaction took place very rapidly, as was evident by the immediate polymer precipitation. The precipitate was filtered and treated with hot toluene and methanol to remove the monomer and initiator residues, followed by vacuum drying.

### Poly(PBBA-co-styrene) Synthesis

The copolymers were prepared through emulsion semibatch (gradual addition of monomers) and batch (single addition of monomers) copolymerization procedures using the formulation given in Table I.

### Kinetic Study

A monomer mixture (1 : 1 weight ratio), emulsifiers, and water were charged into the reactor and stirred

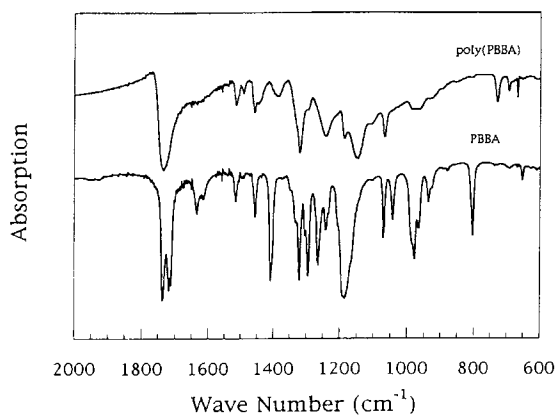
for 45 min, and the initiator was added. Small samples were taken from the reactor and copolymers were precipitated in methanol, filtered, washed with pure water, and dried. The samples were further purified by twice dissolving and precipitating in a toluene-methanol system to remove the unreacted monomer and residual emulsifiers. The final samples were dried under vacuum at 80°C up to a constant weight.

### Solution Blend of Poly(PBBA) and PSt

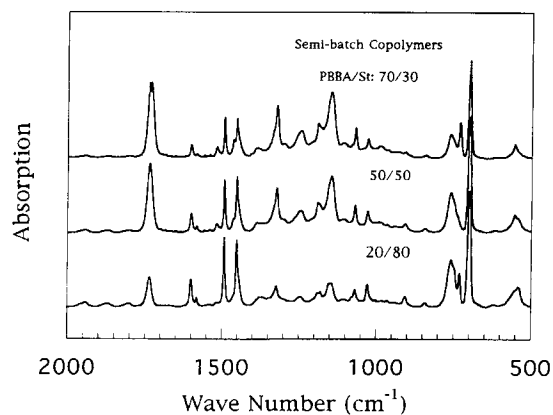
Poly(PBBA) and PSt were codissolved in bromobenzene at 80°C. The blends were obtained by precipitation in methanol, filtering, washing with methanol, and drying under vacuum at 50°C.

### Polymer Analysis

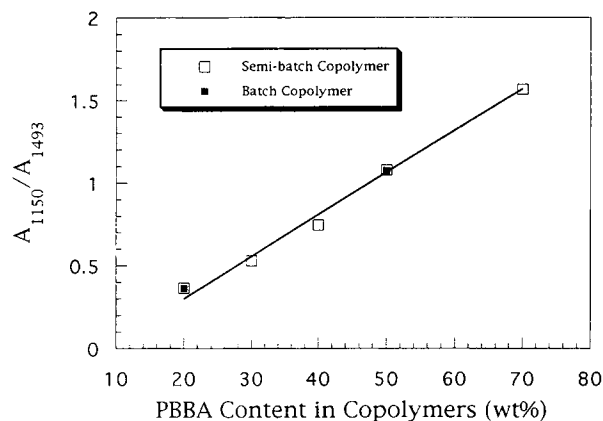
Infrared (IR) analysis was performed using a Mattson 1000 Fourier transform infrared (FTIR) spectrometer. PBBA and poly(PBBA) powders were



**Figure 1** FTIR spectra of PBBA and poly(PBBA).



**Figure 2** FTIR spectra of semibatch copolymers.



**Figure 3** Dependence of  $A_{1150}/A_{1493}$  on PBBA content in semibatch copolymers.

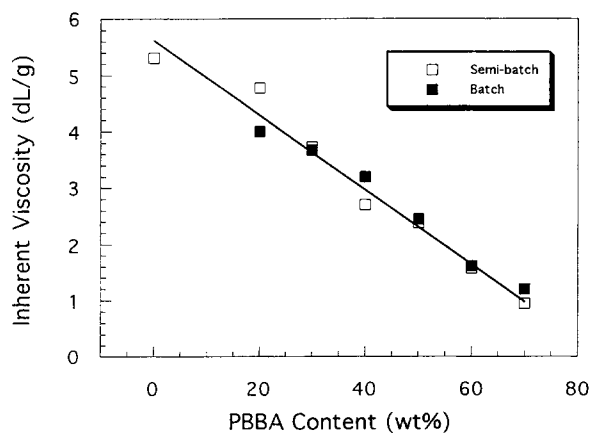
mixed with KBr powder and pressed to form transparent pellets. Copolymer thin transparent films were prepared by casting 0.4% solutions in dichloromethane or toluene onto aluminum plates at room temperature, followed by solvent evaporation.

The inherent viscosity of the copolymers was measured using an Ubbelohde viscometer and 0.5 g/dL toluene solutions at 30°C.

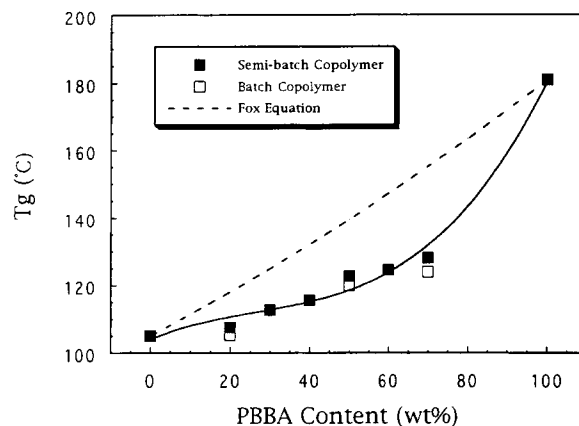
The glass transition temperature ( $T_g$ ) was measured using a Mettler TC 10A DSC. Samples, 12–18 mg, were scanned at a heating rate of 10°C/min under nitrogen. The  $T_g$  values were taken as the transition midpoint of the second run.

Thermal stability was studied using a Setaram TDA92 TGA, at a heating rate of 10°C/min, under air atmosphere.

Specimens, 128 × 12.4 × (1.5–2.2) mm, for mechanical testing, were prepared by compression molding. The mechanical properties were measured



**Figure 4** Effect of PBBA content on inherent viscosity of copolymers.



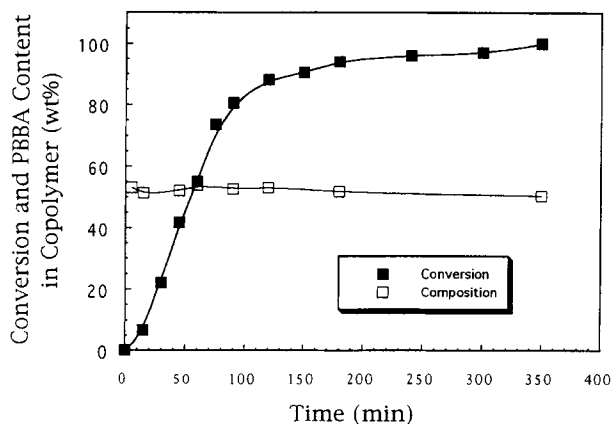
**Figure 5** Effect of PBBA content on  $T_g$  of copolymers.

using a JJ Lloyd, M30K Tensometer at 23°C. The tensile and flexural properties (three-point bending with a 26-mm gauge length) were measured at a crosshead speed of 1.0 mm/min. Reported values represent averages of five specimens tested.

## RESULTS AND DISCUSSION

The FTIR spectra of PBBA and poly(PBBA) are shown in Figure 1. Both the monomer and polymer show typical absorptions at 1150  $\text{cm}^{-1}$  and 1710  $\text{cm}^{-1}$ , reflecting the C—O and C=O stretch of the acrylate moiety, respectively. Absorptions of the vinyl group appear in the monomer spectrum at 980 (*trans* CH wag), 1415 ( $\text{CH}_2$  deformation), and 1650  $\text{cm}^{-1}$  (C=C stretch), etc. (Fig. 1).

The DSC study showed that poly(PBBA) exhibits its  $T_g$  at ca. 180°C; solubility tests revealed that it resists many organic solvents, such as toluene,



**Figure 6** Kinetic behavior of emulsion batch copolymerization: (■) conversion time; (□) composition time.

**Table II**  $T_g$  of Poly(PBBA)/PSt Blends

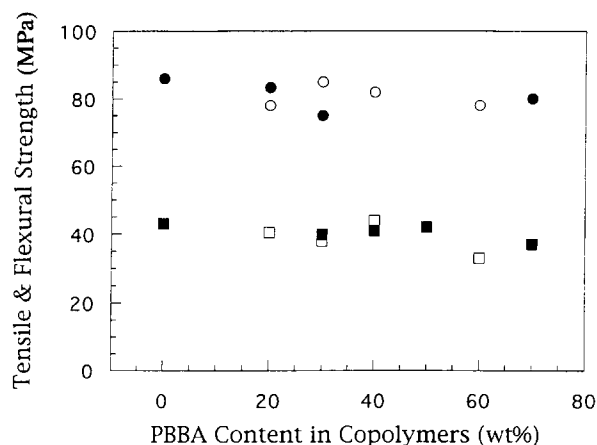
| PBBA Content<br>(wt %) | $T_{g1}$<br>(°C) | $T_{g2}$<br>(°C) |
|------------------------|------------------|------------------|
| 0                      | 105              | —                |
| 30                     | 105              | 180              |
| 50                     | 105              | 181              |
| 70                     | 104              | 181              |
| 100                    | —                | 181              |

xylene, decalin, chloroform, methyl ethyl ketone, dimethyl sulfoxide, dimethyl formamide, etc. Poly-(PBBA) is soluble in hot bromobenzene at ca. 80°C. Compared with the corresponding properties of poly(benzyl acrylate), such as  $T_g$  of 6°C and solubility in toluene,<sup>8</sup> the high temperature and solvent resistant properties of poly(PBBA) are obviously attributed to the pentabromine substitutions in the benzyl group which hinder rotation of the polymer chain.

### Poly(PBBA-co-styrene)

Copolymers of PBBA and styrene at different compositions were synthesized via emulsion semibatch and batch copolymerization methods. The maximum weight percent of PBBA in the monomer feed was 70%, corresponding to the solubility limit of PBBA in warm styrene. The copolymerization period was 6–7 h to ensure full consumption of the monomers. The final latices were stable and the coagula were negligible in all cases. Thus, the copolymer compositions at high conversions were actually determined by the charged monomers' mixture composition.

Figure 2 depicts the FTIR spectra of the semibatch copolymer thin films. The characteristic absorptions of styrene moiety are roughly at 1452 and 1493  $\text{cm}^{-1}$ , reflecting the semicircle stretch and mixed C—H bending of the monosubstituted benzene ring. The characteristic absorptions of the



**Figure 7** Effect of PBBA content on mechanical properties: (●) Flexural strength of semibatch copolymers; (○) flexural strength of batch copolymers; (■) tensile strength of semibatch copolymers; (□) tensile strength of batch copolymers.

PBBA moiety are at 1150 and 1710  $\text{cm}^{-1}$ , reflecting the C—O and C=O stretch, respectively. The relative intensity of the latter two absorptions increased with increasing PBBA content in the copolymers. A good linear relationship is established between the intensity ratio of the 1150 and 1493  $\text{cm}^{-1}$  absorptions and the PBBA content in the copolymer, as shown in Figure 3. This relationship, within the entire studied range of PBBA content (20–70%), is expressed as follows:

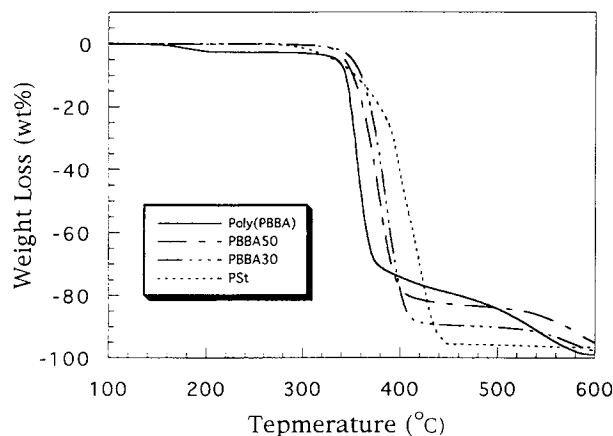
$$A_{1150}/A_{1493} = 0.0247\text{PBBA (wt \%)} - 0.184$$

The reliability of this expression was checked against two batch copolymers having PBBA contents of 20% and 50%, and a good fit was found. Thus this correlation provides a fast and convenient method to estimate the PBBA content in the copolymers.

The inherent viscosity of the copolymers in toluene, a common solvent for the copolymers' composition range studied, linearly decreases with in-

**Table III** Mechanical Properties of Poly(PBBA-co-St) (MPa)

| PBBA Content<br>(wt %) | Semibatch Copolymers |                 | Batch Copolymers |                 |
|------------------------|----------------------|-----------------|------------------|-----------------|
|                        | Young's Module       | Flexural Module | Young's Module   | Flexural Module |
| 0                      | 3450                 | 2480            | 3700             | 3000            |
| 20                     | 3100                 | 2450            | 2990             | 2900            |
| 40                     | 3400                 | 2900            | 3380             | 3650            |
| 60                     | 3800                 | 3100            | 3500             | 3460            |



**Figure 8** Thermogravimetry of homopolymers and copolymers.

creasing PBBA content in both the semibatch and batch copolymers, indicating a molecular weight decrease as shown in Figure 4. This phenomenon, on one hand, is the result of lower reactivity of PBBA, but on the other hand, chain transfer to both PBBA and copolymer may occur, thus terminating the growing chains. The inherent viscosity of the semibatch copolymers is close to that of the batch samples at the same composition.

The  $T_g$  of both the semibatch and batch copolymers as a function of PBBA content (Fig. 5) are practically the same, indicating that the semibatch and batch copolymers possess similar chain structures. Semibatch copolymers normally possess homogeneous molecular structures regardless of the reactivity ratios of the monomers in a "starved" state model of copolymerization, while batch copolymers have a more heterogeneous molecular structure, provided that the reactivity ratios of the monomers are sufficiently different. The finding that the batch copolymers possess random chain structures may indicate that the reactivity ratios of PBBA and sty-

rene are not greatly different, although no data are available to confirm this indication. Figure 5 also shows that the  $T_g$  of both types of copolymers are similar and increase monotonically with increasing PBBA content; thus the copolymers'  $T_g$  is practically independent of the emulsion polymerization process. The  $T_g$  values are lower than those calculated from the Fox equation, which presumably reflects the broad composition and chain length distributions (chains become shorter upon increasing PBBA concentration) characteristic of high conversion copolymers.

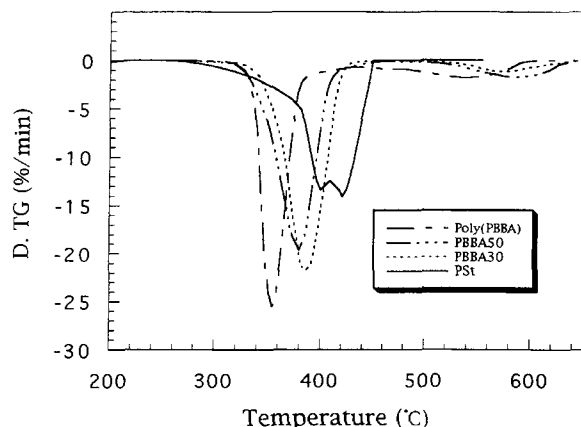
### Kinetic Aspect of Emulsion Batch Copolymerization

The kinetic behavior of the emulsion batch copolymerization process was studied at 1 : 1 wt/wt PBBA/St composition. A linear conversion-time dependency is found between 15 and 75 min. It is known that in batch emulsion copolymerization, the copolymer composition is a function of the monomers ratio, the monomers' reactivity ratios, and the relative solubilities of monomers in water at the reaction temperature.<sup>9</sup> Batch copolymerization produces copolymers with a wide composition distribution where the formed copolymer is richer in the more-reactive comonomer at the initial reaction period and richer in the less-reactive comonomer toward the end of the reaction course, resulting in a heterogeneous chain structure and a so-called "core-shell" particle morphology.<sup>10</sup> The composition drift can be monitored by FTIR analysis at different levels of conversion, as previously reported.<sup>11</sup> In this work, the copolymer composition was also estimated by FTIR at different conversions (reaction time) using the empirical expression suggested above, as shown in Figure 6. The copolymer compositions are close to the monomer compositions and almost constant

**Table IV** Data of Thermal Decomposition

| PBBA Content (wt %) | $T_{i(1\%)}$ (°C) | $T_{i(5\%)}$ (°C) | $T_{d(10\%)}$ (°C) | $T_{dmax}^*$ (°C) | Mass Loss (%) (460°C) |
|---------------------|-------------------|-------------------|--------------------|-------------------|-----------------------|
| PSt                 | 293               | 332               | 354                | 421               | 95                    |
| 30                  | 321               | 350               | 360                | 386               | 87                    |
| 50                  | 323               | 342               | 350                | 378               | 83                    |
| 70                  | 322               | 339               | 347                | 370               | 79                    |
| 100                 | 322               | 341               | 345                | 356               | 77                    |
| b-30                | 319               | 349               | 356                | 397               | 87                    |
| b-50                | 315               | 341               | 348                | 389               | 86                    |

\*  $T_{dmax}$  was determined by DTG.



**Figure 9** DTG curves of homopolymers and copolymers.

along the entire copolymerization course, which apparently stems from similar monomer reactivity ratios. The composition analysis further suggests the relative homogeneity of the batch copolymers' chain structure, like their counterpart semibatch copolymers, thus resulting in properties practically independent of the emulsion copolymerization procedure.

#### Poly(PBBA)/PSt Blends

Blending of fire-retarding additives with other polymers is usually obtained through melt mixing. In this work we studied solution blending, using bromobenzene as a common solvent, to prepare poly(PBBA)/PSt blends containing 30%, 50%, and 70% poly(PBBA). The blends, as expected, exhibit two distinct glass transitions at around 105°C and 180°C, corresponding to the  $T_g$  of PSt and poly(PBBA), respectively, as shown in Table II.

#### Mechanical Properties

The incorporation of low-molecular-weight flame retardants into polymers usually results in a significant drop in the strength properties. Even more, such additives may lower the polymer  $T_g$  and also may migrate to the surface during processing and end use. Thus the use of reactive or polymeric additives could be a practical solution to such shortcomings. In this work, PBBA was copolymerized with styrene acting as an internal flame retardant. The mechanical properties of the presently studied copolymers are summarized in Table III and Figure 7. The Young's and flexural moduli of the copolymers increase slightly with increasing PBBA content (Table III). The copolymer composition does not

remarkably affect the tensile and flexural strengths (Fig. 7). No significant differences in mechanical properties are observed between the semibatch and batch copolymers, which again confirms the similarity in their chain structure. Thus copolymerization of styrene with PBBA is an effective way to enhance the  $T_g$  and fire retardance, without negatively affecting the tensile and flexural properties. It should be noted that normally, roughly 12 wt % bromine content is required to impart flame retardance to a polymer.<sup>12</sup>

#### Thermal Stability

The thermal stability of the copolymers was evaluated by thermogravimetric analysis (TGA) in air. The TGA curves are shown in Figure 8 and the results are summarized in Table IV. Poly(PBBA) degrades rapidly within a narrow temperature range, 340–370°C (mass loss 3–70%), followed by a slow degradation process over a wide temperature range, 370–600°C (mass loss 70–95%). The derived TGA curve (DTG) exhibits two peaks, indicating a two-stage decomposition. The second decomposition stage is possibly attributed to the degradation of the crosslinked residues formed at the first degradation stage. The initial 3 wt % mass loss at ca. 140°C is apparently due to vaporization of residual toluene. Polystyrene has a different degradation behavior: it degrades slowly over a wider temperature range—25 wt % loss in the range of 290–400°C and further loss up to 90% within 400–440°C. The DTG curve of PSt shows a single peak with two shoulders, indicating a single decomposition stage with two different degradation rates, as shown in Figure 9. The initial mass-loss temperature of poly(PBBA) is 322°C, which is higher than that of PSt (293°C), while the decomposition temperature of PSt is 354°C, which is higher than that of poly(PBBA) (345°C), as shown in Table IV. The degradation behavior of the semibatch copolymers is located in between that of the parent homopolymers. The three studied copolymers, with PBBA compositions of 30%, 50%, and 70%, show a two-stage decomposition behavior. Interestingly, the copolymer with 30% PBBA content exhibits a synergistic effect. Its initial decomposition temperature (321°C) is as high as that of poly(PBBA) and its decomposition temperature (360°C) is even higher than PSt (354°C), while the other copolymers do not show this advantage. Poly(PBBA) was also blended with PSt as an external fire retardant and the thermal stability of the blends with 30% and 50% PBBA contents was studied as well. It was found that the decomposition

behavior of a blend was practically identical with a copolymer of the same composition. Since the copolymers are single-phased while the blends exhibit two-phase systems, the thermal stability is clearly not practically affected by the detailed copolymers chain structure.

## CONCLUSIONS

Poly(PBBA) exhibits intrinsic advantages such as high  $T_g$  and solvent resistance. The copolymers obtained from both semibatch and batch emulsion processes show random chain structures, indicating similar reactivity ratios of the two monomers. The inherent viscosity of the copolymers decreases and the  $T_g$  increases with increasing PBBA content, while the mechanical properties are not significantly affected by PBBA content. The structure and properties of the copolymers are practically independent of the emulsion copolymerization procedure. The thermal stability was improved by incorporation of PBBA within certain regions. Blends of poly(PBBA) and PSt showed immiscible phase behavior, with thermal stability similar to the copolymers stability at the same PBBA content.

The partial support of the U.S.-Israel Binational Science Foundation is appreciated. Y.Y. greatly acknowledges the Israel Council for Higher Education for a postdoctoral fellowship. The authors thank Mrs. A. Tzur for the TGA measurements.

## REFERENCES

1. J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, John Wiley & Sons, New York, 1970.
2. J. Troitzsch, *Die Makromol. Chem., Macromol. Symposia*, **74**, 125 (1993).
3. Eur. Pat. Appl. EP 344,700; *Chem. Abstr.* **112**, 199915 m.
4. A. Siegmann, A. Dagan, Y. Cohen, M. Rumack, and P. Georgette, *Int. Conf., Chem. Appl. Bromine and Its Compounds*, D. Price, B. Iddon, and B. J. Wakefield, Eds., Elsevier, Amsterdam, 1986, p339.
5. V. Dave and B. C. Israel, *Polym. Prepr.*, **30**(2), 203 (1989).
6. V. Dave and B. C. Israel, *Polym. Prepr.*, **31**(1), 554 (1990).
7. Eur. Pat. Appl. EP 344,699; *Chem. Abstr.* **112**, 180087w.
8. S. Karause, J. J. Gormley, N. Roman, J. A. Shetter, and W. H. Watanabe, *J. Polym. Sci., Part A-1*, **3**, 3573 (1965).
9. G. E. Ham, R. G. Fordyce, and E. C. Chapin, *J. Polym. Sci.*, **3**, 891 (1948).
10. J. Guillot, European Symp. on Polym. Mater., Lyon, Prepr., 1987.
11. Y. Yuan, A. Siegmann, M. Narkis and J. P. Bell, *Polym. Adv. Tech.*, to appear.
12. M. Narkis, M. Grill, and G. Leeser, *J. Appl. Polym. Sci.*, **13**, 535 (1969).

Received September 14, 1995

Accepted November 27, 1995