

# Thermal Studies on Brominated Atactic Polypropylene

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## SYNOPSIS

Thermal behavior of brominated atactic polypropylene (BAPP), obtained by thermal bromination of atactic polypropylene (APP), was evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). It was found that the initial decomposition temperature (IDT) and char yield increase with the increase in bromine content while integral procedural decomposition temperature (IPDT) showed a decreasing trend. A comparative study of these values in inert and oxidative atmospheres has been made. DTA study shows that onset decomposition temperature (ODT) and glass transition temperature ( $T_g$ ) increase with the increase in degree of bromination. The possible reasons for the occurring phenomena have been discussed.

## INTRODUCTION

Organic bromo compounds have long been recognized as effective flame retardants for polymeric materials, in general. Since thermal decomposition is the first stage in the burning process, the thermal stability of the chemical species responsible for the flame retardation process is obviously an important factor in determining burning characteristics of a compound.

In the present work both thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies have been carried out to evaluate the degradation behavior of various brominated atactic polypropylene (BAPP) samples having different bromine contents. The experiments have been carried out both in nitrogen and air.

It has been found earlier<sup>1</sup> that bromination of atactic polypropylene (APP) leads to an increase in glass transition temperature ( $T_g$ ), higher than that of chloro or sulfochloro derivative.  $T_g$  of BAPP also increases linearly with the increase in bromine content.

## EXPERIMENTAL

BAPP samples were prepared by brominating APP in carbon tetrachloride solution in an all glass reflux system.<sup>2</sup> In the present study, bromination of APP was carried out at 75°C, taking an APP : Br<sub>2</sub> molar ratio of 1 : 2 (with respect to APP mer weight), APP : CCl<sub>4</sub> ratio (w/v) 1 : 100 for different time periods ranging from 30 min to 4 h in order to reach various degrees of bromination. The brominated product was precipitated into methanol. The precipitated BAPP was made free of bromine and hydrogen bromide by several washings with methanol followed by drying at 40°C in vacuum.

Bromine content [in terms of wt % bromine] was estimated using the method of Stepanow.<sup>3</sup>

### Thermogravimetric Analysis

TGA studies were carried out on a DuPont 1090 thermal analyzer having a 951-TG module, both under nitrogen and flowing air. A heating rate of 10°C/min, a sample size of 10 ± 1 mg, and a gas flow of 100 cm<sup>3</sup>/min were maintained.

From the thermograms, initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT) were evaluated.

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**IDT.** The temperature at which the main decomposition of the sample starts after the volatilization of the absorbed water. IDT was obtained from the first point of inflection in the primary thermogram (Fig. 1).

**IPDT.** An index of thermal stability in terms of decomposition temperature, determined from the summation of the whole shape of the primary thermogram, as proposed by Doyle,<sup>4</sup> using the expression

$$\text{IPDT} = A^*(T_f - T_i) + T_i$$

where  $T_f$  = final decomposition temperature,  $T_i$  = initial decomposition temperature, and  $A^*$  = ratio of the area under the curve and the total rectangular area of the curve. In the present studies, IPDT was calculated over the temperature range of 50–600°C.

Char yield was taken as the percentage of solid residue left after heating to 600°C.

#### Differential Thermal Analysis (DTA)

DTA was carried out using a Stanton Redcroft differential thermal analyzer;  $8 \pm 1$  mg of the sample

was heated in air at a heating rate of 10°C/min from ambient temperature to 450°C. From the DTA scan,  $T_g$  (glass transition temperature) and ODT (onset decomposition temperature) were obtained.

## RESULTS AND DISCUSSION

APP on thermal bromination, in absence of any added catalyst, yields brominated product having varying degrees of bromination depending upon the reaction conditions.<sup>2</sup> In APP all the three types of replaceable hydrogen atoms, i.e., primary, secondary, and tertiary are present. In general, the ease of bromination follows the order<sup>2</sup>



So, tertiary hydrogen is most easily replaced followed by the secondary and primary hydrogen.

The products are pale yellow in color and, with increase in degree of bromination, tackiness gradually decreases and finally provides a brittle solid.

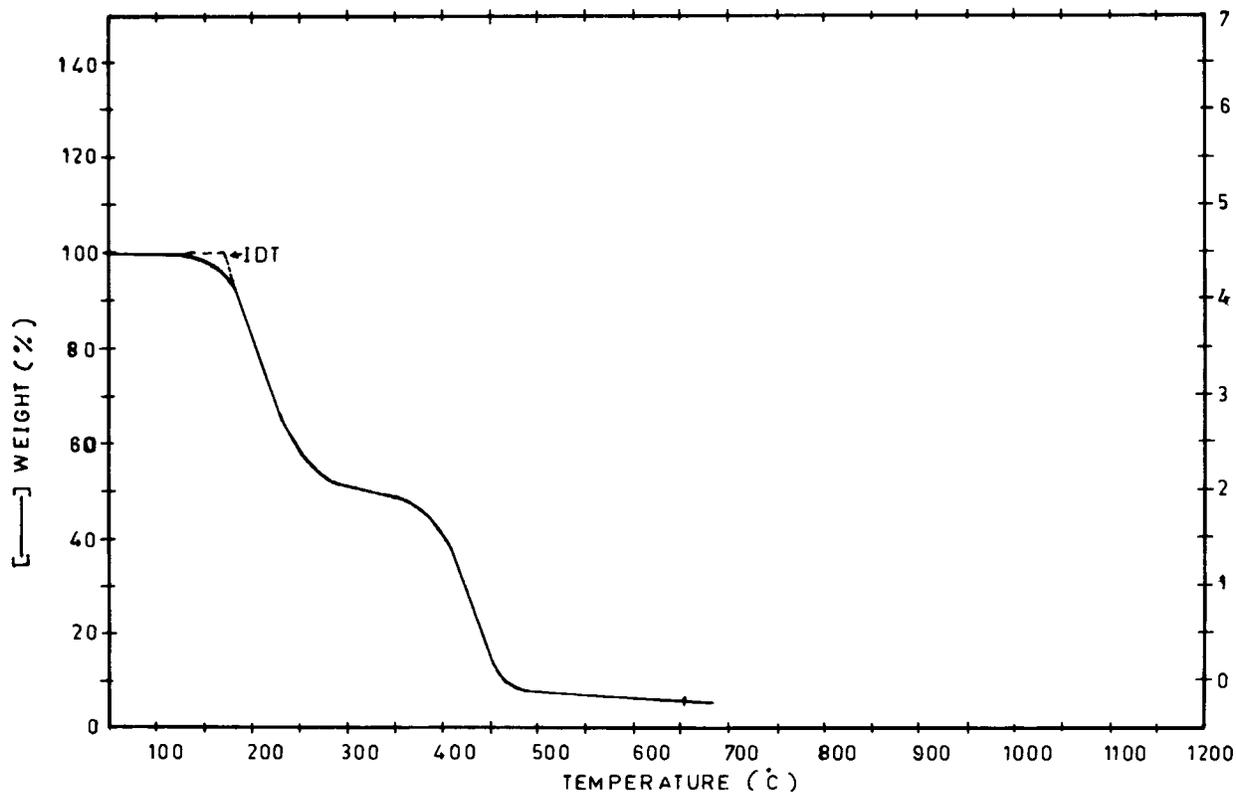
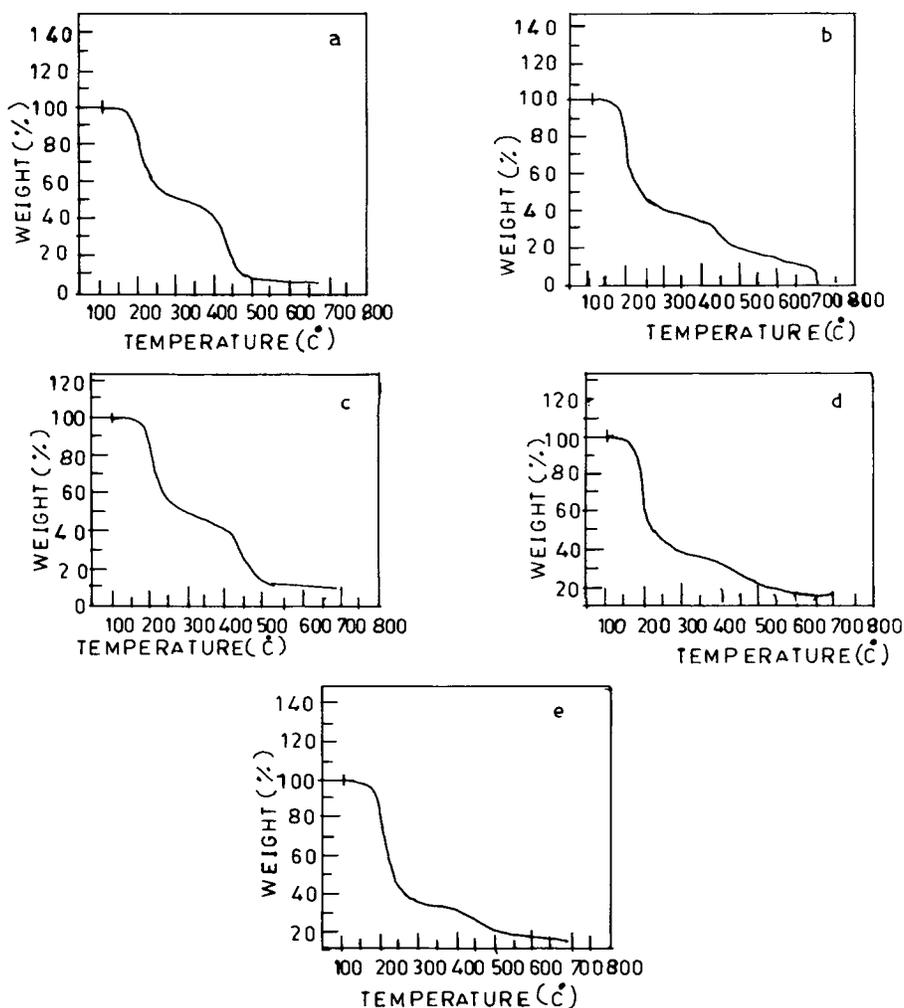


Figure 1 TGA thermogram of BAPP.

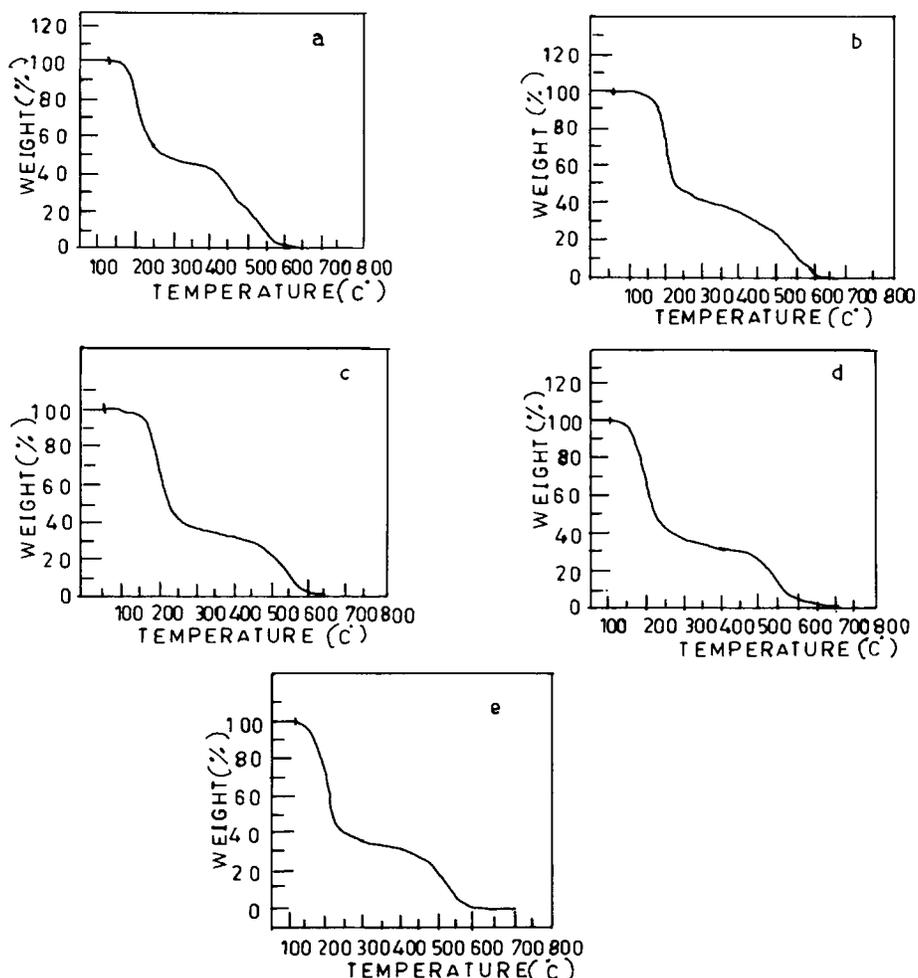


**Figure 2** TGA thermograms of BAPP in nitrogen: (a) 50% Br; (b) 54% Br; (c) 60% Br; (d) 66% Br; (e) 70% Br.

### Thermogravimetric Studies

BAPP samples with varying degree of bromination were analyzed by thermogravimetry both in nitrogen atmosphere and flowing air. The thermograms have been presented in Figures 2 and 3. In general, it can be seen that TG curves (Figs. 2 and 3) for BAPP show that the polymer resembles poly(vinyl bromide) (PVB) in breaking down in two stages.<sup>5</sup> The weight loss in the first stage corresponds to quantitative loss of HBr from the polymer and is referred to as the primary process. Reactions associated with the polyenes, which result from loss of the hydrogen halide, constitute the second stage of thermal degradation process. These include fragmentation and crosslinking of the conjugated polyene structure.

It may also be seen from Figure 4 that, irrespective of the nature of the atmosphere, the IDT values increase continuously with increase in Br content whereas IPDT values decrease. On the other hand, lack of dependence of IDT on the nature of the atmosphere indicates that primary HBr loss and polyene formation take place in a similar sequence in all the atmospheres. Nagy et al.,<sup>6</sup> in the case of poly(vinyl chloride) (PVC) degradation, obtained a similar activation energy of dehydrochlorination in both air and nitrogen. Again, IDT is governed by the ease of decomposition of the weakest bond in a chemical compound. Among the three types of bonds, i.e.,  $\equiv\text{C}-\text{Br}$ ,  $=\text{CH}-\text{Br}$ , and  $-\text{CH}_2-\text{Br}$ , the stability of  $\equiv\text{C}-\text{Br}$  is lowest and hence the decomposition starts at the tertiary C atom. The activation



**Figure 3** TGA thermograms of BAPP in flowing air: (a) 50% Br; (b) 54% Br; (c) 60% Br; (d) 66% Br; (e) 70% Br.

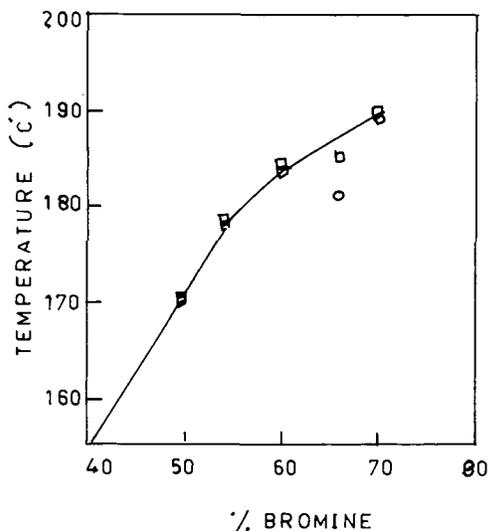
energy values for various types of C—Br bonds decomposition are given below<sup>7</sup>:

	$E_a$ (kcal/mol)
$\text{CH}_3\text{CH}_2\text{Br}$	53.9
$\begin{array}{l} \text{H}_3\text{C} \\   \\ \text{H}_3\text{C}-\text{CHBr} \end{array}$	47.8
$\begin{array}{l} \text{H}_3\text{C} \\   \\ \text{H}_3\text{C}-\text{C}-\text{Br} \\   \\ \text{H}_3\text{C} \end{array}$	41.0

As bromination takes place progressively, more and more secondary and primary H atoms are substituted by bromine, thus increasing the stability of BAPP. Similar results are reported by others also.<sup>8</sup>

It is evident from Figure 5 that IPDT values are higher in nitrogen than in air. This is because, in flowing air, HBr formed by degradation can be removed by air, and degradation is aided by the presence of oxygen thus decreasing IPDT values. However, IPDT values continuously decrease with increasing Br content. This clearly indicates the faster rate of degradation in case of higher brominated samples. This can be attributed to the possible increasing catalytic activity of HBr with its increased formation during degradation.

The autocatalytic effect of HCl evolved in thermal degradation of PVC is well known, and many authors have reported this phenomenon.<sup>9-14</sup> The same process seems to be taking place in the present case. Once the HBr is evolved, it catalyzes the decom-



**Figure 4** Variation of IDT with respect to bromine content in BAPP in N<sub>2</sub> (□) and flowing air (○) atmospheres.

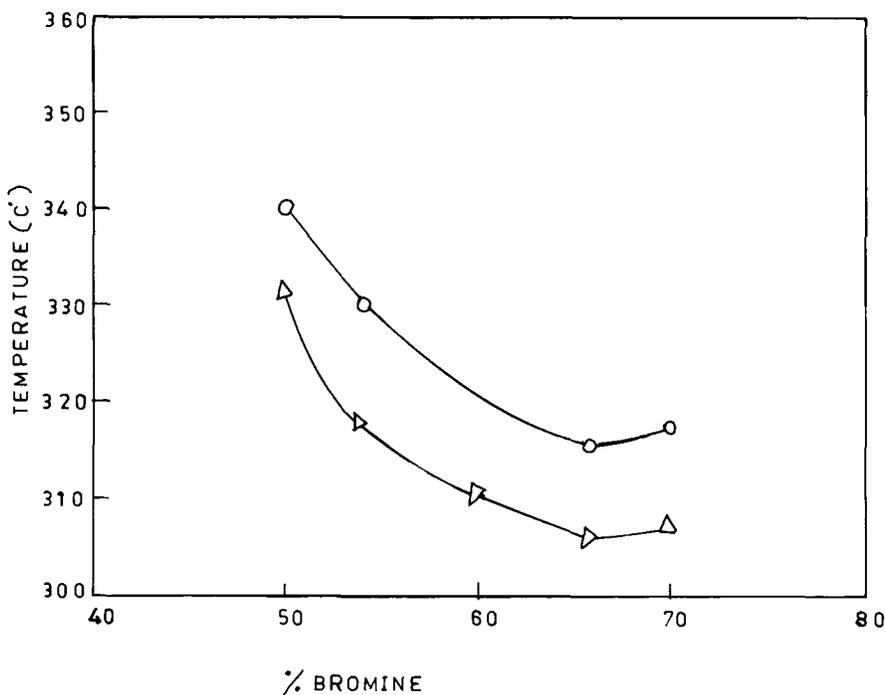
position of BAPP. With increase in Br content, more rapid elimination of HBr over a narrower temperature range takes place to yield a high concentration

of hydrogen bromide which in turn catalyzes the reaction.

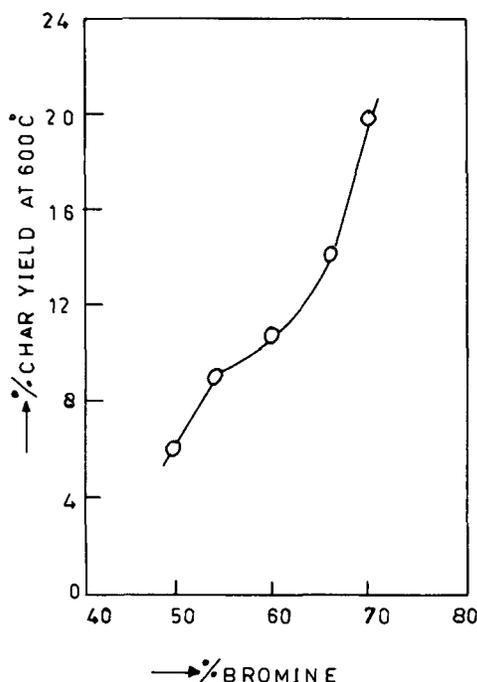
Recent experiments of Shapiro on the thermal decomposition of solid PVC at low conversion in the presence of HCl/HBr over the temperature range 170–210°C demonstrated catalytic activity by both hydrogen halides.<sup>15</sup> Further, HBr is found to have a more pronounced effect as catalyst.

TGA is a powerful method not only to evaluate the pyrolytic residue but also to measure the thermooxidative resistance of the char. The latter is easily accomplished by TG studies in inert and oxidative atmospheres as described in the present work.

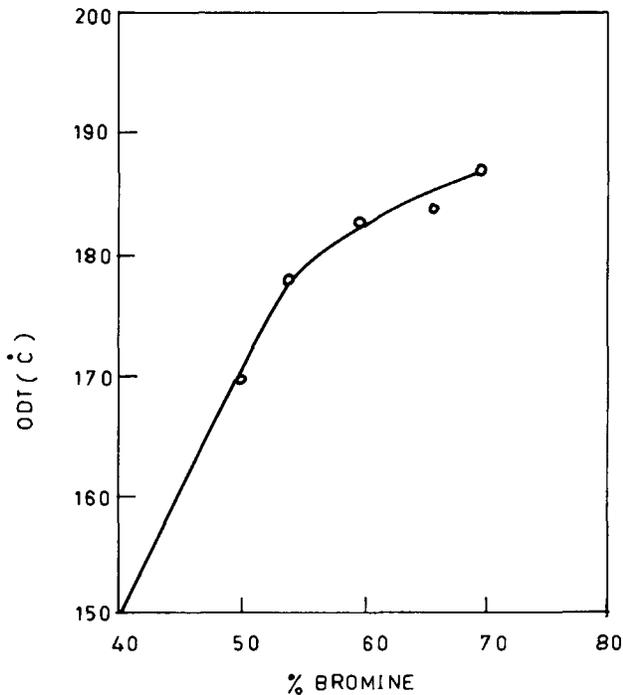
Figure 6 shows the dependence of char yield both on the extent of bromination and the nature of the atmosphere used during degradation. The increase in Br content in the compound leads to an increase in the char as potential volatile content decreases. Practically complete absence of char yield in flowing air shows the increased formation of volatile oxygen containing derivatives. Here, not only are volatiles formed but they get removed by the sweeping atmosphere, thus exposing more surface to further thermooxidative degradation.



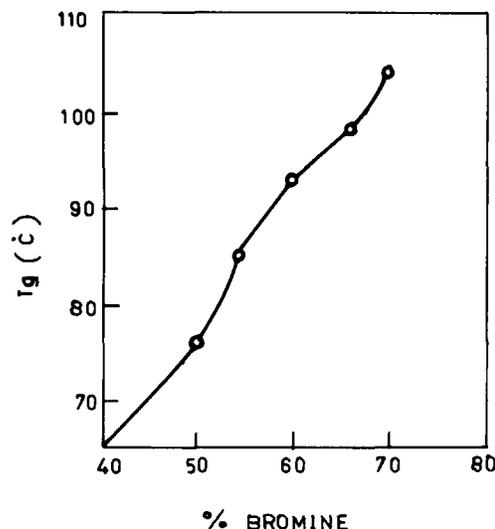
**Figure 5** Variation of IPDT with respect to bromine content in BAPP in N<sub>2</sub> (○) and flowing air (△) atmospheres.



**Figure 6** Variation of char yield with respect to bromine content in BAPP in nitrogen (○) and flowing air (△).



**Figure 7** Variation of ODT with respect to bromine content in BAPP.



**Figure 8** Variation of  $T_g$  with respect to bromine content in BAPP.

#### Differential Thermal Analysis Studies

The onset decomposition temperature (ODT) values of BAPP having different Br content obtained from DTA in presence of air are presented in Figure 7.

The results show that ODT values increase with increase in degree of bromination, confirming results from TG studies.

#### Glass Transition Temperature ( $T_g$ )

Figure 8 presents the variation of  $T_g$  with % bromine content in BAPP. It can be seen from the results that, with the increase in Br content, there is a linear increase in  $T_g$ . Both steric as well as polar effects may be responsible for this behavior. Substitution of Br atoms in APP chain leads to an increase in  $T_g$ , due to the increase of steric hindrance by bulky Br atoms, thus reducing chain mobility. This has also been found by Hartmann and Pinther in the case of chlorinated APP.<sup>16</sup>

In a completely hydrocarbon polymer, such as APP, cohesive energy density (CED) is very low, resulting in very flexible chains, thus showing a  $T_g$  of  $-13^\circ\text{C}$ .<sup>17</sup> With the introduction of bromine in such a structure, mainly in tertiary but the other two positions as well, there is a gradual change from a nonpolar to polar structure. This leads to greater secondary forces between the chains via dipole-dipole interaction and H bonding. In turn, this will be manifested in an increase in CED values and in turn in  $T_g$  values.<sup>18</sup>

## REFERENCES

1. P. Pinther and M. Hartmann, *Wiss. Z. Friedrich-Schiller Univ. Jena, Math.-Naturwiss. Reihe*, **33**, 173 (1984).
2. A. K. Mukherjee and Anita Mohan, *Angew. Makromol. Chem.*, **154**, 99 (1987).
3. J. Urbanski, W. Czerwinski, K. Janicka, F. Majewska, and H. Zowall, *Handbook of Analysis of Synthetic Polymers and Plastics*, Wiley, New York, 1977, p. 42.
4. C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
5. I. C. McNeill, T. Straiton, and P. Anderson, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 2085 (1980).
6. T. T. Nagy, T. Kelen, B. Turcsanyi, and F. Tudos, *Angew. Makromol. Chem.*, **66**, 193 (1978).
7. T. Kelen, *Polymer Degradation*, Van Nostrand Reinhold, New York, 1983, p. 74.
8. A. K. Mukherjee and M. Patri, *J. Macromol. Sci. Chem.*, **A26**, 213 (1989).
9. A. R. Amer and J. S. Shapiro, *J. Makromol. Sci. Chem.*, **A14**, 185 (1980).
10. T. Hjertberg and E. M. Sorvik, *J. Appl. Polym. Sci.*, **22**, 2415 (1978).
11. K. S. Minsker, V. P. Malinskaya, and A. A. Panasenko, *Polym. Sci. USSR*, **15**, 1304 (1970).
12. A. Guyot and M. Bert, *J. Appl. Polym. Sci.*, **17**, 753 (1973).
13. T. Kelen, G. Balint, G. Galambos, and F. Tudos, *J. Polym. Sci.*, **C33**, 211 (1971).
14. E. D. Owen, I. Pasha, and F. Moayyedi, *J. Appl. Polym. Sci.*, **25**, 2331 (1980).
15. K. P. Nolan and J. S. Shapiro, *J. Polym. Sci., Symp.*, **55**, 201 (1976).
16. M. Hartmann and P. Pinther, *Acta Polym.*, **31**, 111 (1980).
17. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York 1975, p. III-144.
18. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1967, p. 67.

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