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Synthesis and Flammability of Bromine-Containing Polybutadiene

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ABSTRACT

COOH-terminated polybutadiene has been converted into COCl-terminated polybutadiene which was further chemically cross-linked with bisphenol-A and tetrabromobisphenol-A. The flammability characteristics of bisphenol-A and tetrabromobisphenol-A resins have been examined using thermogravimetric, ignition temperature and mass burning rate data. Mass burning rate results support that tetrabromobisphenol-A cross-linked polybutadiene is flame retardant compared to the corresponding nonbrominated compositions.

INTRODUCTION

Fire-retardant polymers have vast industrial applications and that is why, during the last decade, a concentrated effort has been made on the synthesis of such polymers. There are two ways to impart fire retardancy to polymers: by the use of additives which are physically mixed with the polymer and by changing the structure of the polymer. The latter, classed as reactive polymers, has the advantage of prolonged sustenance of fire-retardant characteristics unlike the polymer containing physical additives. The general

incorporation of halogens and phosphorus into the polymer chain brings about the fire retardancy. Telechelic polymers having living groups at their ends hold current interest for their applications as space materials and other industrial materials. It was thought to impart fire retardancy into such polymers so that they could find use in some specific applications.

Carboxy-terminated polybutadiene (CTPB) was chosen for the present investigation. The carboxy group was converted into the $-\text{COCl}$ group in the following manner.

SYNTHESIS OF POLYMERS

To CTPB (97.6 g) dissolved in dry benzene (100 mL), thionyl chloride (65 mL; excess) was added and refluxed overnight. Excess thionyl chloride was removed under vacuum. The last traces of thionyl chloride were removed by adding dry benzene (30 mL) and removing the solvent under vacuum. The $-\text{COCl}$ -terminated polybutadiene was obtained in quantitative yield.

This $-\text{COCl}$ -terminated PB was cross-linked with bisphenol-A and tetrabromobisphenol-A. A comparative study was made for the action of bromine on the fire-retardant characteristics of the $-\text{COCl}$ -terminated PB cross-linked with tetrabromobisphenol-A.

DEGRADATIVE STUDIES

Thermogravimetric studies of the cured samples were done in N_2 and O_2 atmospheres. The thermograms are shown in Fig. 1 and the analysis of the thermograms is presented in Table 1.

The thermograms show that the polymer compositions start degrading around 250°C . The degradation is sensitized in the presence of bromine in the samples. The temperature corresponding to the char decomposition is also lowered in the bromine-containing samples. The samples undergo single stage decomposition in both atmospheres. The compositions yield relatively small amounts of char residue. Surprisingly, in oxygen atmosphere it is seen that the bromine-containing sample produces no residue. Both samples start degrading around $250\text{--}290^\circ\text{C}$, but the rate increases only slightly with increasing temperature. For instance, only 5% degradation occurs at temperatures of $500\text{--}550^\circ\text{C}$. This is due to the cross-linked structure of the polymer, where considerable bond scission can occur with low extents of volatilization.

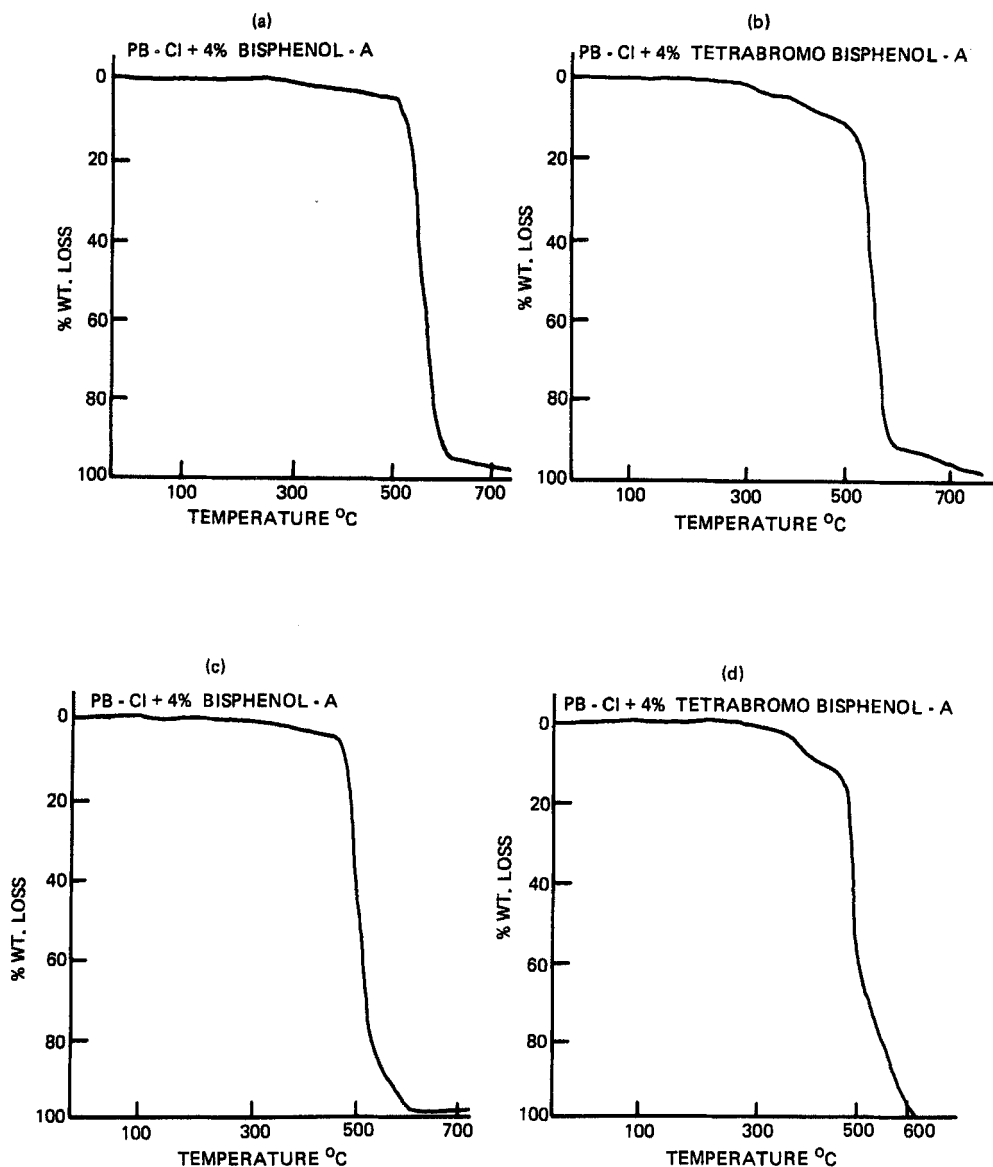


FIG. 1. Thermogravimetric traces of polymers in N_2 (a and b) and O_2 (c and d). Heating rate = $10^\circ C/min$, sample weight = 6.8 mg, gas flow rate = 10 cc/min.

TABLE 1. Analysis of the Thermograms in Nitrogen and Oxygen Atmosphere (heating rate = $10^{\circ}\text{C}/\text{min}$, gas flow rate = $10\text{ cc}/\text{min}$, sample weights = 6-8 mg)

In Nitrogen					
Sample ^a	Temperature ($^{\circ}\text{C}$) corresponding to				Char % at 630°C
	Start of decompo- sition	5% decompo- sition	50% decompo- sition	End of the main decompo- sition	
PB-C1 + 4% bisphenol	260	497	562	609	5
PB-C1 + 4% tetrabromo- bisphenol	256	388	544	588	8
In Oxygen					
Sample	Temperature ($^{\circ}\text{C}$) corresponding to				Final char % (610°C)
	Start of decompo- sition	5% decompo- sition	50% decompo- sition	End of the main decompo- sition	
PB-C1 + 4% bisphenol	293	471	505	605	3
PB-C1 + 4% tetrabromo- bisphenol	248	383	497	620	0

^aPB-C1 = acid chloride terminated polybutadiene.

IGNITION STUDIES

Ignition temperatures were measured on a DTA-type assembly at a high heating rate ($148^{\circ}\text{C}/\text{min}$). A sample of 53 mg was introduced into a platinum cup. The sample was heated at $148^{\circ}\text{C}/\text{min}$ in oxygen atmosphere flowing at $120\text{ cc}/\text{min}$. At the instant of ignition, the flame could be visibly observed. The T and ΔT plots show a sharp deviation which corresponds to the ignition temperature within $\pm 1^{\circ}\text{C}$ accuracy. The ignition temperatures are presented in Table 2. The

TABLE 2. Ignition Temperatures and Mass Burning Rates^a

Sample	Ignition temperature (°C)	Mass burning rate (mg/s)
PB-Cl + 4% bisphenol-A	338	8.8
PB-Cl + 4% tetra-bromobisphenol-A	273	7.6

^a Ignition temperature: Sample weights = 50 mg, O₂ flow rate = 0.22 cm/s, heating rate = 148°C/min. Mass burning rate: sample weights = 390 mg, O₂ flow rate = 1.94 cm/s.

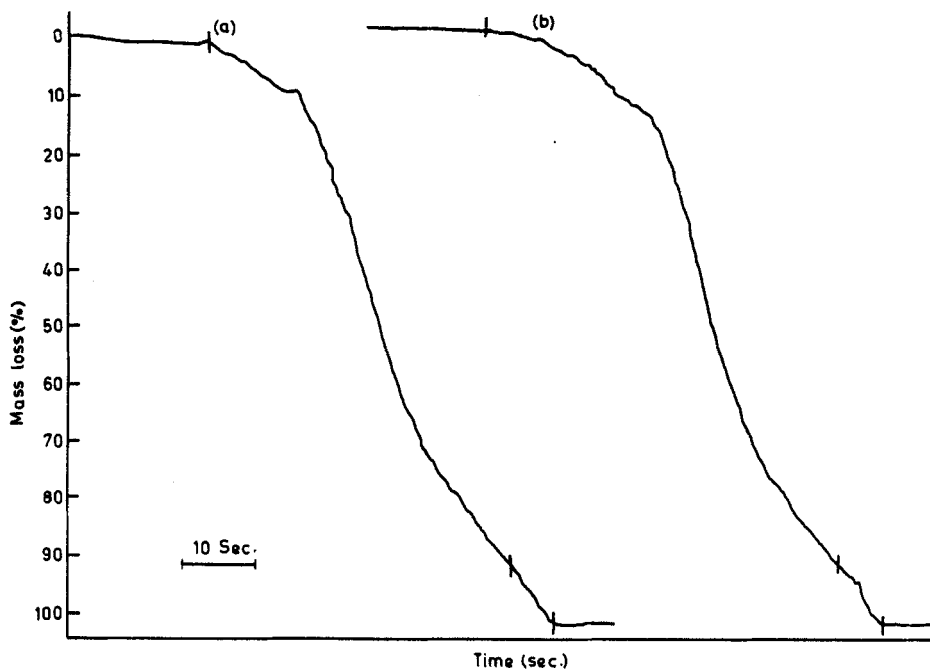


FIG. 2. Mass loss rate curves during the burning of PB-Cl + 4% bisphenol-A (sample weight = 395.5 mg, O₂ flow rate = 1.94 cm/s); (b) PB-Cl + 4% tetrabromophenol-A (sample weight = 388.6 mg, O₂ flow rate = 1.94 cm/s).

presence of tetrabromobisphenol-A decreases the ignition temperature to very low values compared to the nonbrominated composition.

BURNING RATE STUDIES

Mass burning rates of the samples were measured on an LVDT assembly. The details of the assembly are given elsewhere [1]. The loss of weight during burning was continuously recorded using a linear variable differential transducer (LVDT). Samples of ~390 mg were used in the experiment and the burning rates were measured in oxygen atmosphere at a flow rate of 5 L min. The average rates for the overall burning of the samples are also presented in Table 2. The mass loss curves are given in Fig. 2.

Tables 1 and 2 show that while degradation and ignition undergo a sensitization effect in the presence of bromine, the mass burning rates show a desensitization. It is well known that general halogen fire retardants sensitize the thermal degradation [2] and consequently ignition. However, during the burning of a halogen-containing system, the chemical inhibition effects overcompensate for the sensitizing effect on the degradation and bring about an overall desensitizing effect on the burning rate. Since the mass burning rate is a better parameter for characterizing the flammability behavior, one could say that the -COCl terminated polybutadiene cross-linked with brominated bisphenol is a fire retardant as compared to the corresponding nonbrominated composition. It is expected that the addition of small amounts of antimony trioxide might improve the fire-retardant properties further since the synergistic effects of Sb_2O_3 and halogens are well known.

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