

# Thermostabilizing Effect of Copper(II) Bromide on Poly(ethylene oxide) in Their Binary Blends

K. GJUROVA, C. UZOV, A. POPOV, M. ZAGORTCHEVA, G. GAVRAILOVA

Thermal Analysis Section, Central Research Laboratory, University Prof. Dr. As. Zlatarov, 8010 Bourgas, Bulgaria

Received 17 July 1998; accepted 15 May 1999

**ABSTRACT:** Thermoanalytical (thermogravimetry, differential thermogravimetry, and differential thermal analysis) and structural (IR spectroscopy, light microscopy, etc.) methods were employed to estimate the thermal behavior of binary blends of poly(ethylene oxide) (PEO) with copper(II) bromide ( $\text{CuBr}_2$ ) of various concentrations under the conditions of a broad temperature interval. Solid residues obtained after heating the blends at different characteristic stages of the thermal destruction were also studied.  $\text{CuBr}_2$  introduced in concentrations of 5–10% exhibited a significant thermostabilizing effect on PEO in an air medium, regardless of the mode of the blend preparation. No data about the formation of crystallizing complexes or new compounds prepared from the starting materials on heating the blends were obtained within the concentration range studied (0.1–40%  $\text{CuBr}_2$ ). An assumption for the formation of associations between the oxygen atoms of PEO and the metal ion, which obstruct the thermal oxidation processes to a certain degree, were made in order to explain the antioxidative mechanism of action of the inorganic salt. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3324–3330, 1999

**Key words:** poly(ethylene oxide); binary systems; copper(II) bromide; thermostabilizing effect

## INTRODUCTION

Poly(ethylene oxide) (PEO) is known to form ionic complexes (ICs) with some salts of alkaline, alkali-earth, and transition metals that are ion-conducting systems and can be used as solid electrolytes. Consequently, research interests have primarily been associated with the study of both the composition and structure of these systems and their influence on ionic conductivity.<sup>1,2</sup> Such binary systems also possess other valuable properties that have not been completely studied so far. Our studies are currently concerned with the effect of different inorganic metal salts and their

concentration on the thermal properties of PEO, as well as some kinetics phenomena and the overall mechanism of the action of salts.<sup>3,4</sup> Our previous studies and other investigations<sup>5,6</sup> have shown that ICs of these salts at 30–40% content, as well as at very small concentrations, significantly improve the thermooxidative stability of PEO. A number of problems concerning the effect of the ions of metal salts on the thermooxidative PEO destruction, particularly at higher temperatures,<sup>7,8</sup> have to be clarified. More data on the behavior of blends of PEO with various metal salts at different stages of their thermal destruction are necessary from both the theoretical point of view and their further practical applications.

According to previous studies,<sup>9</sup> copper(II) bromide ( $\text{CuBr}_2$ ) forms ICs with PEO that, in turn, suggests its possible influence on both the mass and heat transfer during the process of thermal

Correspondence to: K. Gjurova.  
Contract grant sponsor: University Prof. Dr. As. Zlatarov, Bourgas.

*Journal of Applied Polymer Science*, Vol. 74, 3324–3330 (1999)  
© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/143324-07

oxidation. Therefore, the purpose of this work was to study the influence of different CuBr<sub>2</sub> concentrations on the thermal stability of PEO within a wide temperature range.

## EXPERIMENTAL

### Materials and Sample Preparation

Binary systems of PEO with a mean viscosity molar mass of  $3.2 \times 10^6$  g mol<sup>-1</sup> and CuBr<sub>2</sub> (ch.p.a.) were analyzed. The concentrations of inorganic salt in the mixtures varied from 0.1 to 40 mass %. The samples were prepared in two ways: by mixing the components in the solid state and homogenizing the mixture by grinding at room temperature for 1 h, and by mixing a 1% solution of PEO in methanol with a saturated solution of CuBr<sub>2</sub> in methanol at room temperature and then evaporating the solvent at 50°C under a vacuum.

### Measurements

#### Thermal Analysis

For obtaining thermogravimetry (TG), differential TG (DTG) and differential thermal analysis (DTA) curves a combined dynamic thermal analysis apparatus (OD-102 derivatograph, MOM, Budapest) was used under the following conditions: a heating rate of 6 K min<sup>-1</sup>; a sample initial mass in all experiments of  $0.1 \pm 5 \times 10^{-5}$  g in the form of powder or foil kept in the presence of a drier; a Pt crucible ( $\phi$  9.5 mm) holder; Pt/PtRh thermocouples; no standard substance; medium, air (static) and nitrogen flowing over the sample at a rate of 17 L/h. By using the TG and DTG curves the effective activation energy of the thermal decomposition ( $E_a$ ) of the samples under study was determined.<sup>10,11</sup> Through graphical integration by the weight method, the areas of the total exothermal peaks of the oxidative decomposition were measured and calculated for a 100% thermoactive component ( $\Delta Q$ , %).

The maximum amplitude ( $A_{\max}$ ) of the DTG curve expressed in millimeters was evaluated as a relative measure of the rate of mass loss. The amount of solid residue after heating the sample at a temperature corresponding to the end point of the main destruction step on the TG scans ( $\Delta R_{\text{st}}$ ) and at 500°C ( $\Delta R_{500}$ ) were also determined. These parameters were represented as the percent increase of the residue obtained experimentally, which was related to the theoretically

calculated one on the basis of an assumed additive liberation of volatile matter from the two components of the blend.

### X-Ray Analysis

The X-ray analyses and investigations were carried out on a wide-angle X-ray diffractometer with a goniometer (URD-6, Germany) with a copper anode and K $\alpha$  emission and an Ni filter in an angle interval from 3 to 60 (2 $\theta$ ). The initial components (PEO and CuBr<sub>2</sub>) and their binary mixtures with a CuBr<sub>2</sub> content of 9.4 and 15 mass % unheated and heated at temperatures of 200, 300, 400, and 450°C in air and an inert atmosphere were investigated.

### IR Spectroscopy

IR spectra were registered on a Specord 75 IR instrument (Germany) in a film placed between KBr windows and obtained after the evaporation of methanol or chloroform solvent. The spectra of selected samples were studied prior to and after heating to 200 and 300°C.

### Light Microscopy

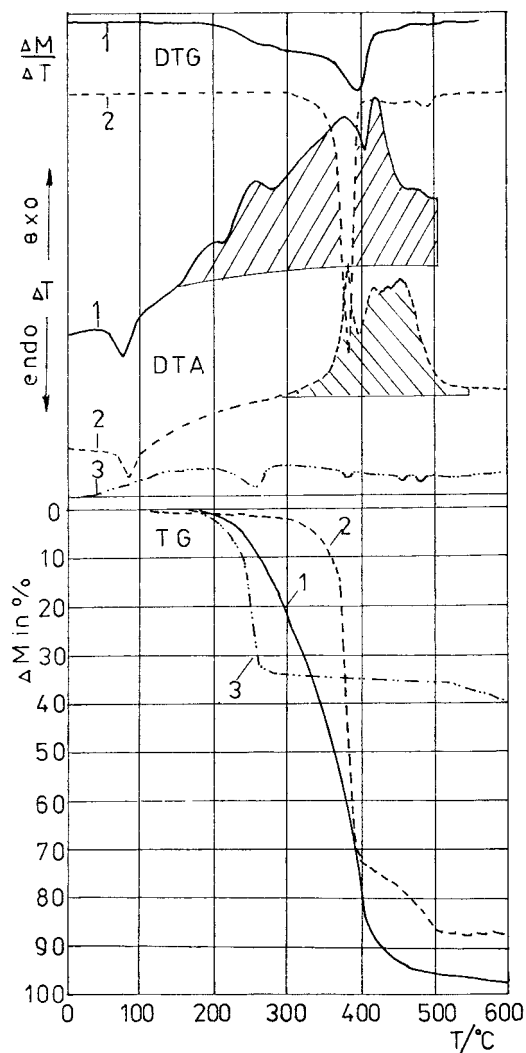
The samples were studied before and after heating to different temperatures by using a Docuval transmission light microscope (Germany) under the conditions of a bright field and polarized light.

## RESULTS AND DISCUSSION

### Thermoanalytical Studies

#### Thermal Behavior of Starting Materials

TG, DTG, and DTA scans of PEO obtained experimentally showed that, with the exception of the endothermic effect of melting the crystalline phase at 75°C, some strong exothermic processes taking place within the whole temperature range of decomposition (180–405°C) in air were predominant (DTA scan, Fig. 1, curve 1). The onset of the first exothermic effect was observed at 150°C with a maximum at 170°C and no visible mass loss under these conditions. The DTG scan showed a two-stage decomposition within the 180–320 and 320–420°C temperature ranges. The initial sample burned out almost completely at 500°C and about 2% solid residue was finally detected.



**Figure 1** Measured curves in air of PEO (curves 1), its blend with 9.4 mass %  $\text{CuBr}_2$  (curves 2), and  $\text{CuBr}_2$  (curves 3).

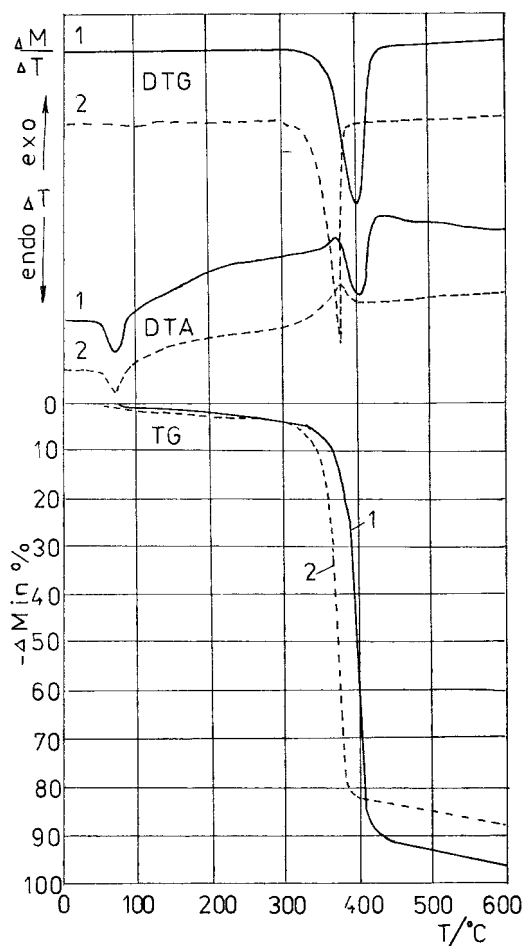
The exothermic oxidation processes were completely counterpoised in the inert medium and the resulting endothermic effect occurred at the stage of the maximum mass loss (Fig. 2, curve 1). The onset of the thermal destruction was shifted by about  $130^\circ\text{C}$  toward higher temperatures as compared to the process in air. At the same time the  $T_{\text{st}}$  and  $\Delta R_{\text{st}}$  remained almost unchanged. Therefore, the same amount of sample underwent one-stage decomposition within a narrow temperature range and the rate of mass loss expressed by the amplitude in the DTG scan  $A_{\text{max}}$  increased significantly. The increase of the thermal stability in the inert medium was also associated with the corresponding increase in the effective

$E_a$  of the total set of decomposition reactions from  $50.5 \text{ kJ/mol}$  in air to  $168 \text{ kJ/mol}$  in nitrogen.

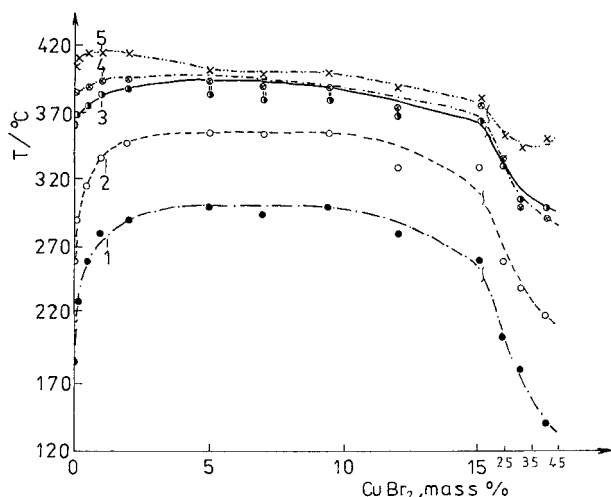
The experimental thermal curves of  $\text{CuBr}_2$  did not depend on the kind of medium in which the heating took place. Decomposition of  $\text{CuBr}_2$  to  $\text{CuBr}$  was observed at the temperature range of  $180\text{--}280^\circ\text{C}$ . The 36% mass loss found experimentally corresponded exactly to the amount of  $\text{Br}_2$  released stoichiometrically as a result of the thermal treatment. Two endothermic effects were observed at  $385$  and  $465^\circ\text{C}$  that were associated with phase transitions. Melting of the salt was recorded at  $490^\circ\text{C}$ , which was followed by decomposition.

#### Thermal Behavior of Binary Blends of PEO and $\text{CuBr}_2$

The mode of the concentration dependencies (Fig. 3) showed that the thermal stability of blends



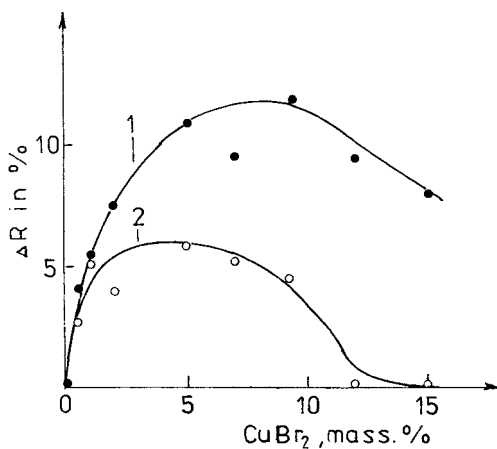
**Figure 2** Measured curves in nitrogen of PEO (curves 1) and its blend with 9.4 mass %  $\text{CuBr}_2$  (curves 2).



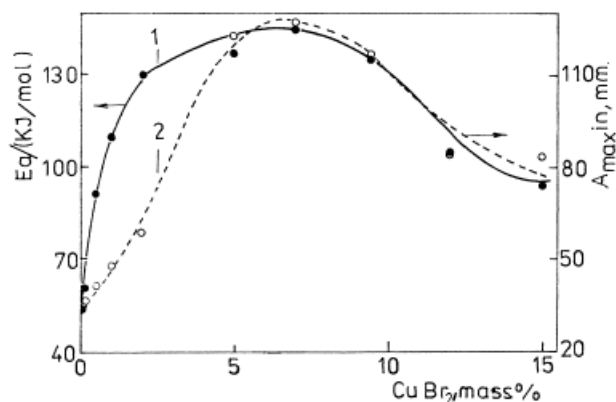
**Figure 3** Thermal characteristics of the binary mixtures of PEO and CuBr<sub>2</sub> from TG curves:  $T_0$ , initial destruction (curve 1);  $T_{10\%}$ , 10% destruction (curve 2);  $T_{50\%}$ , 50% destruction (curve 3);  $T_{\max}$ , maximum rate of destruction (curve 4);  $T_{st}$ , end of first step of destruction (curve 5).

containing from 0.5 to 2 mass % CuBr<sub>2</sub> increased at the highest rate. The temperature values discussed above remained almost unchanged as the salt content increased from 2 to about 10%. The thermal stability deteriorated gradually in the presence of 10–20% CuBr<sub>2</sub>, which was followed by a sharp decrease as the salt content exceeded 20%.

The percent change of the solid residues  $\Delta R_{st}$  and  $\Delta R_{500}$  with the blends of salt content up to 12% was found to be positive (Fig. 4). However,



**Figure 4** Dependence of the residual mass in some characteristics points of TG curves for mixtures of PEO and CuBr<sub>2</sub>:  $\Delta R_{st}$  (curve 1);  $\Delta R_{500}$  (curve 2).



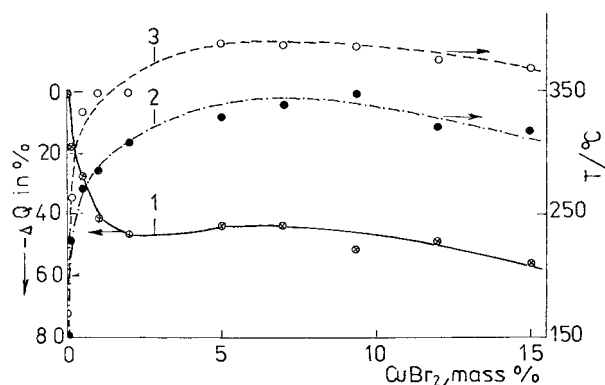
**Figure 5** Dependence of the  $E_a$  of the thermal decomposition (curve 1) and the  $A_{\max}$  (curve 2) of the mixtures on the CuBr<sub>2</sub> content.

the presence of CuBr<sub>2</sub> of content above 15% resulted in the reverse process of formation of unstable matter.

The increase of the initial temperature of decomposition and the amount of solid residue led to the corresponding increase of the effective  $E_a$  for the basic destruction of blends from 50.5 kJ/mol for pure PEO to 148.5 kJ/mol for the PEO/CuBr<sub>2</sub> blend containing 9.4% CuBr<sub>2</sub> (Fig. 5, curve 1).

The discussion conducted so far is supported by the data obtained from the TG curves that showed considerable stabilization of PEO in the air medium in the presence of a certain amount of CuBr<sub>2</sub>. The most pronounced stabilizing effect was observed at the stage of the primary oxidation of the polymer at temperatures reaching the temperature of half-decomposition. The latter, in turn, was found to be almost the same as  $T_{\max}$ . The thermal destruction of the blends containing salt content above 2% occurred in one stage and the values of  $A_{\max}$  increased continuously until the CuBr<sub>2</sub> content reached almost 7% (Fig. 5, curve 2). Therefore, the pattern of changes in both the kinetics and mechanism of the thermal stabilization of PEO in the presence of CuBr<sub>2</sub> was similar to those taking place in an inert medium (Fig. 2, curves 1 and 2). Consequently, a certain antioxidative effect of the salt on the PEO destruction in the air medium was observed.

The antioxidative pattern of the thermal stabilization was confirmed as the temperatures of the initial oxidation ( $T_{ox}$ ) and the first exothermic effect ( $T_{I\ exo}$ ) determined on the DTA curves were compared (Fig. 6, curves 2 and 3). Beside the fast shift of these temperatures toward higher values, some decrease and, finally, disappearance of the



**Figure 6** Dependence of the total heat release by thermooxidative decomposition,  $\Delta Q$  (%; curve 1), of the temperature of initial oxidation  $T_{ox}$  (curve 2) and the temperature of the first exothermal peak  $T_{I_{exo}}$  (curve 3) of the mixtures on the  $CuBr_2$  content.

primary oxidative reactions expressed by the accompanying exothermic effects occurred as the  $CuBr_2$  concentration increased to certain values. The rest of the exothermic effects associated with the decomposition of blends also exhibited changes. The total heat release ( $\Delta Q_{exo}$ ) expressed as the reduced area of the exothermic effects decreased almost by half with respect to the initial PEO as the  $CuBr_2$  content exceeded 1% (Fig. 6, curve 3). The corresponding values remained almost unchanged as the  $CuBr_2$  content changed from 2 to 12%; however, the further increase to 25% resulted in a fast decrease of  $\Delta Q_{exo}$ . This was due to the diminished relative content of the thermoreactive component (PEO) in the blends. Despite this fact, the temperature corresponding to the beginning of oxidation decreased significantly: in such cases the additive ( $CuBr_2$ ) promoted the destruction.

The concentration dependencies of the thermal characteristics on  $CuBr_2$  content showed that, similar to the alkali metals, a thermostabilizing effect on PEO took place and the corresponding function had a maximum. However, no thermostabilizing effect of  $CuBr_2$  was observed at its higher concentrations (30–40%), which was different from the behavior of the alkali metal salts under the same conditions. This difference is believed to be associated with both the composition and stability of the corresponding IC.<sup>3</sup> No melting of another crystalline phase was recorded on the thermoanalytical curves of the compositions studied with the exception of the melting peak of PEO itself at about 75°C for both the powdery and film samples.

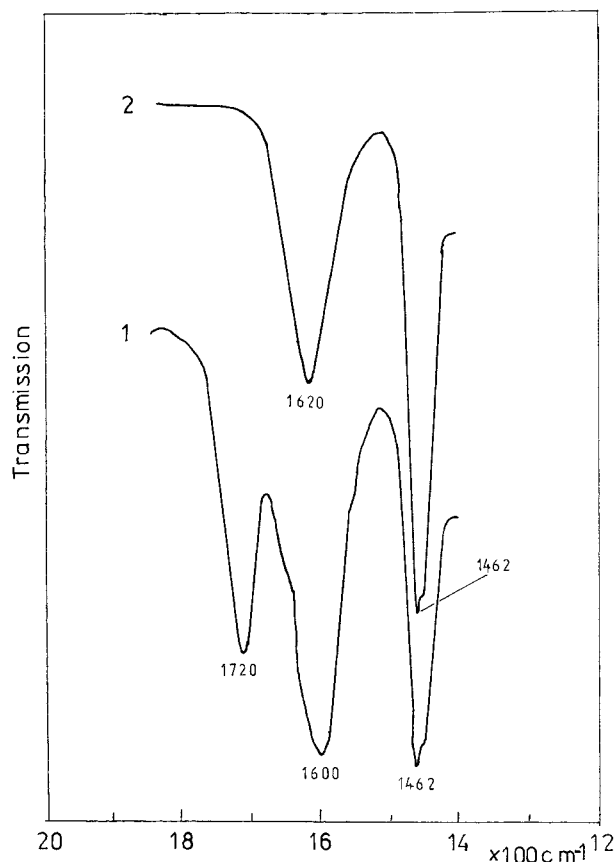
The comparison of the results obtained on heating the powders and films led to the observation that films with a salt content up to 10% had visibly higher thermal stability than the corresponding powdery samples. A better homogeneity of films, as well as a decreased contact surface with the oxidation medium, are believed to be the possible explanation of this phenomenon. Generally, however, the extent of the thermostabilizing effect of  $CuBr_2$  on PEO in air was almost entirely determined by the salt concentration in the blends with no practical significance of the mode of the blend preparation.

### Spectroscopic, X-Ray, and Microscopic Studies

The course of the thermal curves do not unambiguously provide information concerning the mechanism of the thermostabilizing effect of  $CuBr_2$  on the polymer, neither does it throw light on the exact mode of formation and mutual influence of the high-temperature solid residues obtained after heating. No possible associations between PEO and the salt could be proved at the stage of blend preparation or during the heating. Therefore, further studies were deemed necessary to explain the results obtained.

The IR spectra of the pure PEO treated thermally at 300°C showed additional absorption bands  $\nu_{(C=O)}$  at 1720  $cm^{-1}$  and a broad band at about 1600  $cm^{-1}$  resulting from the formation of various oxidation products.  $CuBr_2$  as an inorganic compound of symmetrical structure does not exhibit any absorption in the IR region. The absorption band at 1462  $cm^{-1}$   $\{\delta(CH_2)\}$  was selected as an internal standard and, accordingly, the corresponding absorption ratios  $A_{1720}/A_{1462}$  and  $A_{1600}/A_{1462}$  of PEO and its blend containing 9.4%  $CuBr_2$  were compared after heating the samples to 300°C (Fig. 7, curves 1, 2). Under these conditions a significant reduction, especially of the  $A_{1720}/A_{1462}$  absorption ratio, was observed. The band at 1600  $cm^{-1}$  was also observed with non-heated PEO and its blends prepared by 1-h vigorous grinding but was not detected with the non-ground PEO. In this case the band at 1600  $cm^{-1}$  is believed to result from a low-temperature mechanically initiated oxidative destruction.

The residues obtained after heating at 400–450°C were nontransparent for the IR beam because of the high carbon content. The X-ray diffraction pattern of these residues showed a decrease in the intensity of corresponding maximums, which is typical for PEO, with the



**Figure 7** IR spectra of PEO, heated at 300°C (curve 1) and a mechanical blend of PEO and 9.4 mass % CuBr<sub>2</sub> heated at 300°C (curve 2).

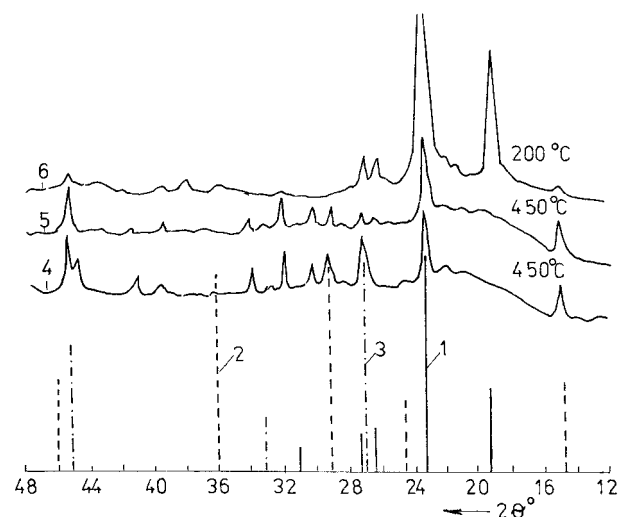
exception of the maximum at  $2\theta = 23.3^\circ$ . The latter was significantly preserved under these conditions (Fig. 8, curves 4 and 5). Some maximums typical for the starting CuBr<sub>2</sub> (14.8, 28.9, and  $46.1^\circ 2\theta$ ) were also preserved and new maximums ( $27.1$  and  $44.9^\circ 2\theta$ ), which are characteristic for the crystalline phase of CuBr<sub>2</sub>, appeared. The X-ray patterns of the residues obtained from the starting components and preheated separately to the temperatures mentioned above showed an almost complete disappearance of the diffraction maximums. This confirmed the assumption for a mutual stabilization of the components in the blends without any chemical interaction.

The blends with the highest thermal stability contained 5–10% salt and exhibited a significantly higher relative intensity of the diffraction maximums preserved in the solid residues from the starting compounds. Besides, the X-ray patterns of the solid residues from the blends with these concentrations did not depend on whether

the heating occurred in air or nitrogen. Thus, once again the antioxidative mode of the stabilizing effect of CuBr<sub>2</sub> was confirmed.

The observation of nonheated blends by using the light microscopy method showed the formation of aggregations between the two components with an improved contact after PEO melting. These aggregations were partially preserved up to temperatures of about 400°C but underwent destruction at 450°C, which was confirmed by the data from the TG scans. Good homogenization and mutual penetration of the components are believed to render the appropriate conditions for the formation of associations at the molecular level. These associations are likely to be formed on the basis of “blockage” of the partial negative charge at the oxygen atom of PEO by the metal from CuBr<sub>2</sub>, thus leading to the mutual stabilization of the components observed experimentally. The latter is believed to retard the primary oxidation processes associated with heating the system and catalysis of the chain reactions of decomposition at the higher temperatures.

The analyses of the solid residues obtained at different stages of heating also showed that no chemical interactions between the starting materials occurred. The assumption for the formation of crystallizing or amorphous ICs with blends of about 9.4% CuBr<sub>2</sub> content was not confirmed.



**Figure 8** Wide-angle X-ray diffractograms: starting PEO (curve 1); starting CuBr<sub>2</sub> (curve 2); CuBr<sub>2</sub> heated at 450°C (curve 3); mechanical mixture (9.4 mass % CuBr<sub>2</sub>) heated at 450°C (curve 4); foil (9.4 mass % CuBr<sub>2</sub>) heated at 450°C (curve 5); mech mixture (9.4 mass % CuBr<sub>2</sub>) heated at 200°C (curve 6).

## CONCLUSIONS

1. By means of both the thermoanalytical and structural methods employed, copper(II) bromide was found to exhibit a significant thermostabilizing effect on PEO in an air medium when introduced in optimum concentrations of 5–10%. This effect did not have a considerable dependence on the mode of introduction of the inorganic salt into the polymer.
2. The thermostabilizing effect of the salt is believed to have an antioxidative pattern as a result of the formation of associations between the oxygen atoms within the polymer chains and the metal ion that, in turn, isolates the oxygen from the oxidation medium.
3. No data on the formation of any crystallizing ionic complexes between the components in the blends were obtained within the whole concentration range (0.1–40% CuBr<sub>2</sub>) studied. The assumption for the formation of an amorphous complex of a composition corresponding to the ratio of PEO/CuBr<sub>2</sub> of 90.6 : 9.4 was not confirmed.
4. According to the experimental data obtained, no chemical reactions that could

result in the formation of new compounds on heating the blends took place.

## REFERENCES

1. Wright, P. V. *J Macromol Sci* 1989, A26, 519.
2. Kudaibergenov, S. E.; Ushanov, W. J.; Tcherdabaev, A. S.; Ismagulova, S. S.; Bekturov, E. A. In *Chimija Monomerov i Polimerov*; Kazach, A. N., Ed.; Nauka: Alma Ata, Kazakhstan, 1988; p 119–134.
3. Gjurova, K.; Bogdanov, B.; Uzov, C.; Zagortcheva, M.; Gavrailova, G. *Thermochim Acta* 1997, 296, 37.
4. Bogdanov, B.; Zagortcheva, M.; Gjurova, K.; Popov, A. *J Appl Polym Sci* 1998, 70, 995.
5. Oguru, J.; Matsui, H. *Jpn. Pat.* 24582, 1963.
6. Johnson, A. C.; Iinks, C. G. *U.S. Pat.* 3,634,305 1972.
7. Cameron, G. G.; Ingram, M. D.; Qurechi, M. Y.; Gearing, H. M.; Costa, L.; Camino, G. *Eur Polym J* 1989, 25, 779.
8. Jones, G. K.; Farrinton, G. C. In *Int Symp on Polym Electrolytes*, 1989; Department of Chem Engineering, University of Pennsylvania: Philadelphia, PA, 1990; 2nd ed., p 239–250.
9. Vincent, C. A. *Prog Solid State Chem* 1987, 17, 145.
10. Reich, L.; Lee, H. T.; Levi, D. W. *J Polym Sci* 1966, B1, 535.
11. Gjurova, K. M. Ph.D. Thesis, Sofia, Bulgaria, 1986.