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THERMOANALYTICAL STUDIES OF RUBBER OXIDATION: STABILIZATION OF NATURAL RUBBER BY TWO HEXADENTATE MACROCYCLIC LIGANDS

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ABSTRACT

The effects of two hexadentate macrocyclic ligands, 1,4,7,10,13,16-hexathiacyclooctadecane and 1,4,10,13-tetrathia-7,16-diazacyclooctadecane, on metal ion catalyzed oxidation of natural rubber have been studied by DSC. Both ligands show antioxidant activity and are able to suppress oxidation catalyzed by copper, iron, cobalt and manganese ions. The two hexadentate ligands are better metal ion deactivators than a tetradentate ligand 1,4,7,11-tetrathiocyclotetradecane.

INTRODUCTION

Many polymers undergo thermal oxidation during fabrication, storage and their end use. The oxidation of polymers is manifested by discoloration, changes in surface appearance and the loss of mechanical properties. The presence of unsaturation in natural rubber makes it particularly susceptible to oxidation. Transition metal ions such as copper, iron, manganese and cobalt catalyze the oxidation of polymers. To protect polymers against metal ion catalyzed oxidation, suitable chelating agents are added to deactivate the ions by forming inactive complexes [1,2].

The chemistry of macrocyclic ligands and their complexes has received considerable attention in recent years [3–5]. The macrocyclic complex shows an enhanced stability as compared with the similar non-macrocyclic complex. We have reported the use of six macrocyclic ligands to stabilize natural rubber against metal ion catalyzed oxidation [6–8]. Five of the ligands are tetradentate and they are, in general, less effective in inhibiting the catalytic effects of metal ions of co-ordination number six such as manganese and cobalt. The other ligand, 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, is hexadentate but is not an effective inhibitor. Since crown ether (oxygen-containing macrocyclic ligand) has been found to be an ineffective inhibitor [8], it will be of interest to study the effectiveness of hexadentate nitrogen and

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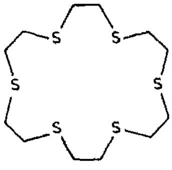
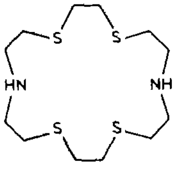
sulfur macrocyclic ligands. In this communication, we report the thermoanalytical study of the inhibition of metal ion catalyzed oxidation of natural rubber by two hexadentate macrocyclic ligands 1,4,7,10,13,16-hexathiacyclooctadecane (S6) and 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (S4N2).



(S6)



(S4N2)

EXPERIMENTAL

Materials

Natural rubber of pale crepe grade was used. It was purified by extraction with acetone for 24 h and subsequent precipitation of the benzene solution of the extracted rubber in methanol.

The naphthenates of copper, iron, manganese and cobalt were obtained from K and K Laboratories, Inc.

Ligands S6 and S4N2 were prepared according to the method of Black and McLean [9].

Equipment

A Perkin–Elmer DSC-4 differential scanning calorimeter was used. The instrument was purged with oxygen at a flow rate of 50 ml $\min^{-1}$ during operation.

Sample preparation

Appropriate amounts of purified natural rubber, metal naphthenate and macrocyclic ligand were dissolved in benzene separately. The solutions were then mixed and droplets of solution were placed in the DSC sample pan and allowed to dry in a vacuum oven at room temperature.

The amount of metal naphthenate used was 0.2 g per 100 g of rubber, and the amount of macrocyclic ligand used was 0.0025 mol per 100 g of rubber.

Evaluation of activation energy and induction time

The activation energy of oxidation (E_a) was evaluated by the Kissinger method [10] based on the oxidation exotherm peak temperature (T_p) at five different heating rates of 5, 10, 20, 40 and 60 K min^{-1}. For isothermal study, the sample was brought to 400 K with a heating rate of 320 K min^{-1} and the time required for the appearance of the oxidation peak was taken as the induction time (t_i).

RESULTS AND DISCUSSION

Thermoanalytical techniques are widely used to study rubber oxidation [11–13]. The oxidative stability of rubbers and the effectiveness of antioxidants can be evaluated by DSC based on the heat of oxidation (ΔH_{ox}), the activation energy of oxidation (E_a), the isothermal induction time (t_i), the initial onset temperature of oxidation (T_i) and the oxidation exotherm peak temperature (T_p). Since DSC requires only a small amount of material, it is particularly useful in the present study as macrocyclic ligands were obtained in very low yields.

Tables 1–3 show the effects of macrocyclic ligands on E_a, T_p and t_i. Higher values of E_a, T_p and t_i indicate a better oxidative stability. The measurements of the catalytic effects of transition metal ions and the effectiveness of 1,4,8,11-tetrathiacyclotetradecane (S4) were repeated and compared with the previous results [8]. The E_a values obtained in the present study are slightly higher than those in the previous study. This is because of the use of a different batch of natural rubber in these studies. Nevertheless, the implications of the results remain the same. Manganese and cobalt ions produce more pronounced catalytic effects than those of copper and iron ions, and the tetradentate ligand S4 is less effective in inhibiting the catalytic effects of the former two ions.

TABLE 1

Effects of macrocyclic ligands on activation energy of oxidation (E_a) of natural rubber

Metal ion	E_a (kJ mol^{-1})			
	Blank	S4	S6	S4N2
Blank	82	97	100	98
Copper	75	87	90	93
Iron	71	89	90	93
Manganese	65	82	89	88
Cobalt	58	83	91	96

TABLE 2

Effects of macrocyclic ligands on oxidation exotherm peak temperature (T_p) of natural rubber

Metal ion	T_p [a] (K)			
	Blank	S4	S6	S4N2
Blank	438	440	446	444
Copper	431	433	433	442
Iron	429	431	432	439
Manganese	425	429	436	440
Cobalt	417	429	435	446

[a] Heating rate, 5 K min^{-1}.

Both ligands S6 and S4N2 possess antioxidant activity as shown by the higher values of E_a, T_p and t_i for natural rubber containing these ligands than that for natural rubber without any additive. The results also show that the hexadentate ligands possess better antioxidant activity than that of the tetradentate ligand S4. The antioxidant mechanism of macrocyclic ligands has not been elucidated. However, many nitrogen compounds such as arylamines and sterically hindered amines, and sulfur compounds are widely used as polymer stabilizers and their antioxidant mechanism has been well established [2].

The most significant result as shown by the values in Tables 1–3 is the ability of ligands S6 and S4N2 to stabilize natural rubber against metal ion catalyzed oxidation. One of the main functions of metal ion is to catalyze the decomposition of hydroperoxides by one-electron transfer redox reactions to give chain propagating radicals [1]

$$ROOH + M^{n+} \rightarrow RO^{\bullet} + OH^{-} + M^{(n+1)+}$$

$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\bullet} + H^{+} + M^{n+}$$

Chelating agent can deactivate the ion by forming an inactive or stable complex. The effectiveness of the chelating agent depends on its ability to

TABLE 3

Effects of macrocyclic ligands on isothermal induction time (t_i) of natural rubber at 400 K

Metal ion	t_i (min)			
	Blank	S4	S6	S4N2
Blank	28	39	130	44
Copper	12	19	24	28
Iron	6	9	21	22
Manganese	4	9	23	25
Cobalt	2	10	25	34

complex the ion, as well as the coordination number of the ion. It has been found that tetradentate ligands such as S4, are in general unable to suppress completely the catalytic effect of ions with coordination number six, as only four of the coordinating sites of the ion are blocked by the ligand [8]. The present study shows that ligands S6 and S4N2 are able to suppress completely the catalytic effects of cobalt and manganese ions. Thus a macrocyclic ligand which is able to block all the co-ordinating sites of the ion is an effective metal deactivator.

It is noted that ligand S4N2 is a slightly better metal deactivator than ligand S6. In the study of the effects of various chelating agents on copper-catalyzed oxidation of polypropylene, the effectiveness of a chelating agent appears to be related to the stability constant of the copper complex [1]. It will be of interest to see if there is a correlation between the effectiveness of a macrocyclic ligand and the stability constant of its complex. However, other than for the copper complex of S4 which has a stability constant of 2.2×10^4 in 0.1 M $HClO_4$ solution at 298 K [14], information is not available for comparison.

In summary, the present series of studies evaluates the effectiveness of eight macrocyclic ligands as antioxidants for natural rubber. Ligands containing nitrogen and sulfur possess antioxidant activity, and a hexadentate ligand is a better metal ion deactivator than a similar tetradentate ligand. However, the use of macrocyclic ligands as antioxidants for polymers is not practical because they can only be obtained in very low yields.

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REFERENCES

1 Z. Osawa, in G. Scott (Ed.), Developments in Polymer Stabilization, Vol. 7, Elsevier, London, 1984, Chap. 4.
2 N. Grassie and G. Scott, Polymer Degradation and Stabilization, Cambridge University Press, Cambridge, 1985, Chaps. 4 and 5.
3 C.J. Pederson, in R.M. Izatt and J.J. Christensen (Eds.), Synthetic Multidentate Macrocyclic Compounds, Academic Press, New York, 1978, Chap. 1.
4 G.A. Melson, in G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979, Chaps. 1 and 2.
5 R.M. Izatt, J.S. Bradshaw, S.A. Nielson, J.D. Lamb, J.J. Christensen and D. Sen, Chem. Rev., 85 (1985) 271.
6 S.H. Goh and Y.B. Lim, Thermochim. Acta, 32 (1979) 81.
7 S.H. Goh, A.S. Ng and P.S. Kok, J. Rubber Res. Inst. Malays., 30 (1982) 45.
8 S.H. Goh, Polym. Degrad. Stab., 8 (1984) 123.

9 D.St.C. Black and I.A. McLean, Aust. J. Chem., 24 (1971) 1401.
10 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
11 D.W. Brazier, Rubber Chem. Technol., 53 (1980) 437.
12 J.J. Maurer, in E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, Academic Press, New York, 1981, Chap. 6.
13 A.K. Sircar, J. Sci. Ind. Res., 41 (1982) 536.
14 L.S. Sokol, L.A. Ochrymowycz and D.B. Rorabacher, Inorg. Chem., 20 (1980) 3189.