

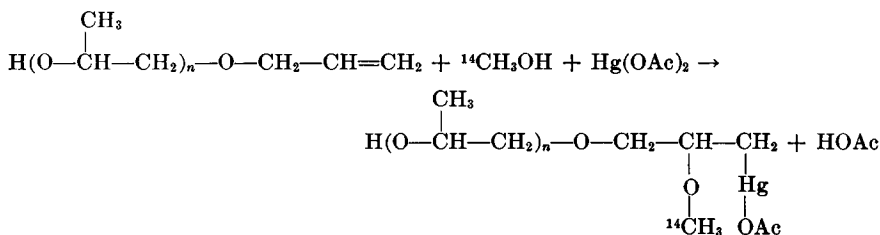
## NOTES

**Radiochemical Determination of Unsaturation in Cyclic Oxide Polymers in Presence of Antioxidants**

## INTRODUCTION

Elastomers prepared by copolymerizing propylene oxide with an unsaturated epoxide represent a new class of specialty rubbers offering unusual low temperature flexibility, good ozone and heat resistance, and excellent dynamic properties over a wide temperature range.<sup>1</sup> A unique characteristic of these copolymers which distinguishes them from hydrocarbon elastomers is partial solubility in many polar solvents; methanol, for example, may extract up to 70% of a typical copolymer.<sup>2</sup> Determination of unsaturation in the products by halometric methods, such as the widely employed iodine monochloride technique,<sup>3,4</sup> requires removal of the antioxidant used or application of relatively large empirical corrections for halogen absorption by the inhibitor. Although antioxidants may be largely removed from hydrocarbon polymers by dissolving them in a good solvent and precipitating in methanol, the unusual solubility characteristics of poly(alkylene oxide) elastomers preclude use of this method of purification. An analytical technique is thus desirable which will permit determination of low concentrations of ethylenic unsaturation in cyclic oxide polymers without interference from the common inhibitors.

Unsaturation in copolymers of propylene oxide and unsaturated epoxides may be determined using the technique described previously for the determination of trace concentrations of double bonds of both the allyl and *cis*-propenyl ether types in poly(propylene oxide) glycols.<sup>5</sup> Treatment of a solution of the polymer in ethylene dichloride with excess methanol-<sup>14</sup>C and mercuric acetate yields the *vicinal*-methoxy-<sup>14</sup>C-acetoxy-mercuri derivative of the double bond. The reaction is illustrated for a terminal allyloxy group arising in the base-catalyzed polymerization of propylene oxide.<sup>5-7</sup>



Excess methanol and ethylene dichloride are removed in a current of inert gas. Residual radioactivity, corrected by a blank analysis, is proportional to the unsaturation in the specimen and is determined by wet combustion of the residue. The labeled carbon dioxide formed is assayed by the ionization chamber-electrometer method. Use of the combustion flask as reaction container obviates isolation and purification of the radioactive polymer.

## EXPERIMENTAL

Dilution, purification, and radioassay of methanol-<sup>14</sup>C by wet combustion after conversion to the *p*-nitrobenzoate are described elsewhere.<sup>5</sup> Specific activity of the methanol used for the analysis of cyclic ether polymers was 0.2 to 0.4  $\mu\text{Ci}/\text{mmole}$ .

Polymer specimens of  $30 \pm 3$  mg were weighed into the 10-ml round-bottom combustion flasks, which were fitted with 28/15 ball-and-socket joints for attachment to the

wet combustion apparatus. The specimen was dissolved in 3 to 4 ml of dried and distilled ethylene dichloride. The solution of mercuric acetate in methanol-<sup>14</sup>C was prepared by dissolving 500 mg of the reagent-grade salt in 3.3 ml of methanol-<sup>14</sup>C with gentle warming. One ml of this reagent was added to the sample flask and a 28/15 socket cap was clamped to the flask. The flask was swirled gently until a homogeneous solution was obtained, after which the flask was immersed in an oil bath at 40°C for 1 hr. Removal of ethylene dichloride and excess methanol-<sup>14</sup>C, wet combustion of the residue, and assay of the radioactive carbon dioxide were performed as described previously.<sup>6</sup> Blank determinations were made using the same amounts of solvent and reactants employed in the analysis of polymers. In addition, a quantity of the antioxidant used in the polymer was added in an amount equivalent to that present at the level of 1% in a 30-mg specimen, together with 0.02 to 0.04 mmole of acetic acid. The acetic acid was omitted in the analysis of propylene oxide homopolymers. Benzoic acid, 20 mg, was added to the blank flasks before combustion to reduce formation of free oxygen.

### RESULTS AND DISCUSSION

The double bond content of the polymer is obtained from the following expression:

$$\text{Unsaturation, mmole/g} = \frac{A_T - A_B}{SW}$$

TABLE I  
Effect of Type and Amount of Antioxidant on Unsaturation

Sample number	Antioxidant present	Antioxidant content, % of specimen	Unsaturation, <sup>a</sup> mmoles/g
1	Phenyl-β-naphthylamine (PBNA)	0.42	1.50 <sup>b</sup>
		3.83	1.50
		7.34	1.49
		11.8	1.49
		18.4	1.52
2	4,4'-Methylenebis-(2,6-di- <i>tert</i> -butylphenol)	0.51	0.46, 0.46
		4.53	0.46
		7.05	0.45
		9.94	0.40
		15.4	0.38
3	2,6-Di- <i>tert</i> -butyl-4-methylphenol	1.0	1.23, 1.20, 1.20
		3.6	1.22
		7.5	1.20
4	Nickel dibutyldithiocarbamate	1.2	0.92
		9.5	0.90
5	Nickel dibutyldithiocarbamate	1.2	0.96
		7.8	0.97
6	2,2'-Methylenebis-(4-methyl-6- <i>tert</i> -butylphenol)	0.5	1.59, 1.59
		1.5	1.59, 1.58, 1.59
		5.4	1.65
		8.2	1.70
		11.8	1.79

<sup>a</sup> Unsaturation of the polymer fraction only.

<sup>b</sup> Average of 19 determinations having a standard deviation of 0.015 mmole/g.

Radioactivity present in blank analyses is equivalent to 0.04 to 0.09 mmoles of unsaturation per gram referred to a specimen weight of 30 mg. Typical residual activities for different lots of methanol with the several antioxidants used are given in Table II.

TABLE II  
Effect of Type and Amount of Antioxidant on Blank Activity

Antioxidant present	% Antioxidant* in polymer	Methanol- <sup>14</sup> C lot	Sp. act. of metha- nol, $\mu$ Ci/mmole	Residual act., nCi	No. of analyses	Blank unsat., <sup>a</sup> mmoles/g
Phenyl- $\beta$ -naphthylamine	0.4	A	0.253	0.69 $\pm$ 0.02	3	0.091
	0.5	B	0.378	0.99 $\pm$ 0.07	3	0.087
	1.0	C	0.188	0.37 $\pm$ 0.05	3	0.065
4,4'-Methylenebis- (2,6-d- <i>tert</i> -butylphenol)	1.0	A	—	0.72 $\pm$ 0.05	3	0.095
	1.0	A	—	0.50 $\pm$ 0.01	4	0.066
	1.0	B	—	0.60 $\pm$ 0.05	3	0.053
2,2'-Methylenebis- (2,6-di- <i>tert</i> -butylphenol)	1.0	C	—	0.21 $\pm$ 0.01	3	0.039
	0.5	A	—	0.40 $\pm$ 0.03	3	0.053
	0.5	B	—	0.89 $\pm$ 0.03	3	0.078
0.5	C	—	—	0.33 $\pm$ 0.04	3	0.058
	1.0	C	—	0.24 $\pm$ 0.01	3	0.042

\* Based on a 30-mg. specimen.

where  $A_T$  is total activity present in sample flask, in  $\mu\text{Ci}$ ;  $A_B$  is average activity present in blank flasks, in  $\mu\text{Ci}$ ;  $S$  is specific activity of the methanol- $^{14}\text{C}$ , in  $\mu\text{Ci}/\text{mmole}$ ; and  $W$  is weight of sample, in grams.

The method described uses to advantage the solubility characteristics of cyclic oxide polymers which make separation of the antioxidants difficult, i.e., the significant solubility of these elastomers in polar solvents. The methoxymercuration reaction, which is most rapid in pure methanol, is quantitative within 1 hr at  $40^\circ\text{C}$  for cyclic oxide elastomers in a 1:4 methanol:ethylene dichloride solvent mixture. Increasing the reaction time to 2 hr did not yield higher unsaturation values. Pendant double bonds introduced using butadiene monoxide, allyl glycidyl ether, crotyl glycidyl ether, vinyl cyclohexene monoxide, and other unsaturated epoxides as comonomers have been determined without interference from residues of the coordination catalyst employed.<sup>1</sup> Attachment of the methoxy- $^{14}\text{C}$  group to the penultimate carbon of terminal double bonds reduces steric effects and permits quantitative determination of comonomers such as vinylcyclohexene monoxide.

The principal advantage of the radiochemical technique over halometric methods for unsaturation is relative freedom from interference by common antioxidants in the amounts used in normal compounding practice. Table I gives the results of analyses of representative elastomers in the presence of different amounts of typical antioxidants used for stabilization.

A comparison of unsaturation values observed with representative polymers by the radiochemical method and a titrimetric procedure is provided in Table III. The titrimetric technique employed pyridine sulfate dibromide with catalysis by mercuric acetate.<sup>9</sup> Results reported for the polymers containing PBNA were corrected for bromine absorption by the inhibitor, which was determined by ultraviolet spectrophotometry.<sup>10</sup>

TABLE III  
Comparison of the Radiochemical Method with a Titrimetric  
Method for Unsaturation in Cyclic Oxide Polymers

Sample number	Antioxidant present	Anti-oxidant content, <sup>a</sup> %	Unsaturation, mmoles/g		Relative deviation, <sup>a</sup> %
			Titrimetrically	Radiochemically	
7	Phenyl- $\beta$ -naphthylamine	0.08	1.27	1.21 1.20	-5.1
8			1.53 1.54	1.50 1.48	-2.9
9		0.06	1.09	1.09	0.0
10			1.10	1.09	
11		0.06	1.17	1.19	0.0
			1.22	1.18	
12	2,6-Di- <i>tert</i> -butyl-4-methylphenol	0.5	1.15	1.18	+3.0
			1.15	1.19	
13		0.5	2.24	2.17	-2.0
			2.20	2.18	
14		0.5	1.24	1.22	-1.6
			1.24	1.22	
15		0.5	0.80	0.78	-3.1
			0.80	0.77	
			0.95	0.93	-2.1
			0.97	0.97	

<sup>a</sup> Deviation of radiochemical from titrimetric results.

No correction of titrimetric results was made in the case of 2,6-di-*tert*-butylphenol, since bromine absorption by this antioxidant under the conditions of analysis was negligible.

Sensitivity and precision of the radiochemical method are determined by the ratio of the blank activity to that of the sample, as well as by the reproducibility of both measurements. In the common range of 0.5 to 1.5 mmole/g of double bond in stabilized cyclic oxide elastomers, sensitivity and precision of the isotopic technique are comparable to those of titrimetric methods. Accuracy of methoxy-<sup>14</sup>C-mercuration, however, is superior to that of conventional halogenation procedures, due to the significantly lower antioxidant response. The radiochemical method, in addition, is applicable to microamounts of elastomer.

Because the method described is more time consuming and, in general, less practicable than conventional techniques for measuring polymer unsaturation, its principal value lies in its usefulness as a reference technique for the analysis of cyclic oxide polymers containing significant amounts of antioxidants which exhibit marked halogen absorption.

#### References

1. E. E. Gruber, D. A. Meyer, G. H. Swart, and K. V. Weinstock, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**(3), 194 (1964).
2. J. G. Hendrickson, A. E. Gurgiolo, and W. E. Prescott, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**(3), 199 (1963).
3. T. S. Lee, I. M. Kolthoff, and E. Johnson, *Anal. Chem.*, **22**, 995 (1950).
4. W. Cooper, G. A. Pope, and G. Vaughan, *European Polym. J.*, **4**, 207 (1968).
5. D. R. Campbell, *Microchem. J.*, **13**, 630 (1968).
6. L. E. St. Pierre and C. C. Price, *J. Amer. Chem. Soc.*, **78**, 3432 (1956).
7. G. J. Dege, R. L. Harris, and J. S. MacKenzie, *J. Amer. Chem. Soc.*, **81**, 3374 (1959).
8. D. M. Simons and J. J. Verbanc, *J. Polym. Sci.*, **44**, 303 (1960).
9. R. G. Rowe, C. C. Furnas, and H. Bliss, *Ind. Eng. Chem., Anal. Ed.*, **16**, 371 (1944).
10. F. W. Banes and L. T. Eby, *Ind. Eng. Chem., Anal. Ed.*, **18**, 535 (1946).

D. R. CAMPBELL

The General Tire & Rubber Co.  
Akron, Ohio 44309

Received September 9, 1969

Revised October 29, 1969