Polymer Bulletin 6, 375–380 (1982)

Polymer Bulletin

Phase Transfer Catalyzed Reactions on Polymers

5. Degradation of Polyepichlorohydrin with Superoxide*

Antoni S. Góźdź**

Institute of Organic and Polymer Technology, Technical University of Wrocław,
PL-50370 Wrocław, Poland

ABSTRACT

Linear high-molecular weight polyepichlorohydrin elastomer (PECH) was reacted with potassium superoxide in benzene and benzene-dimethylsulfoxide solutions in the presence of 18-crown-6 as a phase-transfer catalyst. Elemental analysis, spectroscopic studies, and viscosity measurements showed that superoxide ion attacks both the chloromethyl group leading to the formation of various oxygen-containing groups, and main chain, causing its rapid degradation. A reaction mechanism has been proposed which appears to be dependent on the solvent.

INTRODUCTION

During the past decade, several synthetically useful reactions of superoxide anion, $O_2^{\bar{\cdot}}$, with various organic substrates under phase transfer catalyzed conditions have been reported (WEBER and GOKEL 1977, STARKS and LIOTTA 1978, DEHMLOW and DEHMLOW 1980). Most of these studies have been carried out on low molecular weight alkyl halides (SAN FILLIPO et al. 1975, JOHNSON and NIDY 1975, ROBERTS and SAWYER 1981) and esters (SAN FILLIPO et al. 1976, GIBIAN et al. 1979), which afforded the corresponding dialkyl peroxides or alcohols, or alcohols and acids, respectively, with minor amounts of elimination and oxidation side-products.

In two recent papers, OSAWA et al. (1979, 1981) have reported reactions of superoxide ion with polymeric substrates, namely, poly(vinyl chloride) and poly (vinyl alcohol). Although these reactions proceeded in the absence of catalysts, and in the former tetrahydrofuran was used as a solvent whose reaction with $O_2^{\bar{\cdot}}$ was not precluded, the results obtained indicate that the resultant polymers contain a number of oxygen-containing functional groups. Moreover, in the case of poly(vinyl alcohol) substantial molecular weight decrease occured.

---

*Part 4: A.S. Góźdź, Polymer Bull. 5, 591 (1981)

**Present address: Textile Research Institute, P.O. Box 625, Princeton, NJ 08540, USA

0170-0839/82/0006/0375/$01.20

The purpose of the present work was to study the reaction of high molecular weight polyepichlorohydrin (PECH), which was used previously for preparation of poly(propylene oxide) substituted on the methyl groups (SCHACHT et al. 1978), with superoxide ion, in the pressence of phase transfer catalyst in aprotic solvents.

EXPERIMENTAL

Materials

Commercial polyepichlorohydrin (PECH, Hydrin 100, B.R. Goodrich Chemical Co.) was purified by precipitation from its benzene solution into a large excess of methanol followed by washing with methanol and drying at 40°C i. vac. for 48h. The polymer had an intrinsic viscosity, $[\eta]$, of 1.176 dl/g, at 25°C in toluene and a chlorine content of 38.4% (theor. 38.42%).

Benzene (POCh, Gliwice), tetrahydrofuran (THF; POCh, Gliwice), and dimethylsulfoxide (DMSO; Reachim, Moscow) were refluxed several hours over calcium hydride and distilled. Methanol (POCh, Gliwice, reagent grade) and potassium superoxide (KO_2; 96.5% pure) of Alfa-Ventron, U.S.A. were used as received. 18-Crown-6, (1,4,7,10,13,16-hexaoxacyclooctadecane) was synthesized according to GOKEL et al. (1974).

Reaction Procedure

A 250-ml flat-bottomed reaction vessel capped with a rubber septum with a nitrogen inlet and outlet, and fitted with a magnetic stirrer was charged with dry dimethylsulfoxide (55 ml), benzene (75 ml), and polyepichlorohydrin (1.85 g, 20 mmole). The contents of the vessel were stirred in order to dissolve the polymer. In a seperate reaction flask, powdered potassium superoxide (0.148 g, 2 mmole) and 18-crown-6 (0.528 g, 2 mmole) were stirred for 5 min in 20 ml of DMSO, then the contents while stirring were added to the first flask. After the predetermined time the polymer was precipitated into a large excess of vigorously stirred methanol containing 5 vol-% of a 0.05 M HCl solution. The polymer was washed with methanol, dissolved in benzene, reprecipitated into methanol, and dried i. vac. at room temperature for 48 h.

Measurements

Infrared spectra were recorded on a Specord IR-71 spectrophotometer as films cast from benzene solutions onto sodium chloride plates. Ultraviolet spectra were obtained for solutions of the polymer (10 mg/10ml) in THF using 1-cm cells and a Specord UV-VIS spectrophotometer. Viscosity determinations were carried out with an Ubbelohde-type viscometer at 25°C in toluene using 0.100 % (w/v) solutions. The intrinsic viscosity values were calculated from single-point determinations using the formula $[\eta] = (\ln t_c/t_o)/c$ which may be applied for $t_c/t_o \leq 1.15$ and $c \leq 0.1\%$. Chlorine analyses were carried out in an oxygen-filled flask (DIXON 1969).

Results and Discussion

PECH contains two potentially reactive sites in its structure, namely the chloromethyl groups and the ether linkages, of which only the former were expected to react with superoxide ion. However, preliminary experiments showed that a considerable decrease in molecular weight occurs when the reaction medium contains DMSO, as indicated by a decrease in intrinsic viscosity of the polymer (Table 1). This decrease proceeds differently in the absence of DMSO, since a slight increase in intrinsic viscosity initially observed is followed by a slow decrease (Table 1).

TABLE 1

Degradation of polyepichlorohydrin with superoxide ion[a)]

Sample No.	Solvent	Catalyst Presence	React. Time, Min.	Chlorine Content, wt.%	$[\eta]$25° tol.
PECH start.		-	-	38.40	1.14
1	Benzene	+	5	37.55	1.17
2		+	15	38.35	1.04
3		+	60	38.67	0.383
4		-	60	35.00	1.35
5	Benzene DMSO 1:1	+	60	32.46	0.076
6		-	60	33.26	0.123

a) PECH (0.465g, 5 mmole) dissolved in 50 ml of solvent(s), stirred at R.T. with KO_2 (36 mg, 0.5 mmole) and 18-crown-6 (132 mg, 0.5 mmole)

Elemental analysis of the degraded polymers showed a decrease in chlorine content. The data indicate that superoxide ion causes a chlorine loss in PECH as expected, the loss being faster in DMSO and in the presence of 18-crown-6. These data indicate that superoxide ion attacks both the chloromethyl group as well as the main chain composed of oxyalkylene units.

In order to specify the kind of functional groups formed in the reaction of PECH with KO_2, infrared spectra of the polymers obtained were recorded for films. Essentially, the only new bands observed for degraded PECH were those at 3450 cm^{-1} and those within a 1640-1740 cm^{-1} region (Figure 1). The remaining part of the spectrum was unchanged when compared with that for the unreacted polymer. A strong band at ca. 3450 cm^{-1} was observed only for the samples obtained in the presence of DMSO; it was assigned to ν_{O-H}. Two strong bands appearing at 1640 and 1740 cm^{-1}, and a weak band at 1680 cm^{-1} can also be seen. A band at 1740 cm^{-1} was assigned to νC=O and that at 1640 cm^{-1} to νC=CH$_2$. A small absorption at 1680 cm^{-1} remains unassigned, although it seems likely that it is caused by carbonyl absorption of an α-chloromethyl ketone.

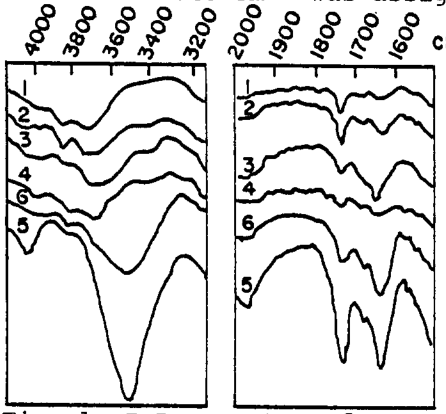
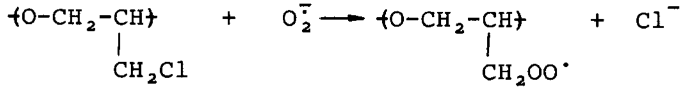


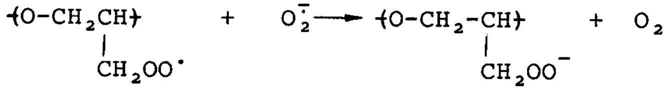
Fig. 1, I.R. spectra of samples of degraded PECH listed in Tab. 1

Ultraviolet spectrum of the degraded PECH showed several bands at 240-270 μm, but no assignments could be made.

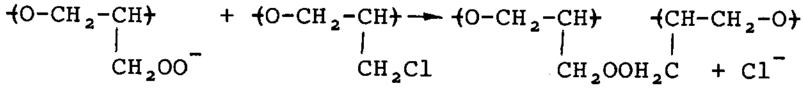
The results of previous studies on reactions on alkyl halides with superoxide ion as well as the results presented in this communication allow us to propose the following series of reactions proceeding on the chloromethyl group of PECH when potassium superoxide and 18-crown-6 are used in benzene:



$$-\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2Cl}}{\underset{|}{\mathrm{CH}}})\!- \;+\; \mathrm{O_2^{\overline{\cdot}}} \longrightarrow -\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2OO^{\cdot}}}{\underset{|}{\mathrm{CH}}})\!- \;+\; \mathrm{Cl^-} \qquad (1)$$

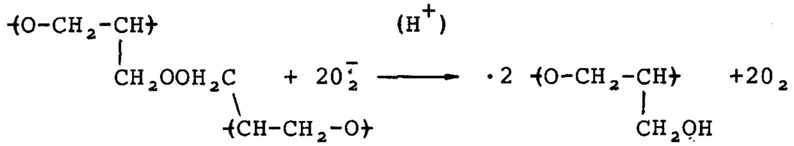


$$-\!(\mathrm{O{-}CH_2}\underset{\mathrm{CH_2OO^{\cdot}}}{\underset{|}{\mathrm{CH}}})\!- \;+\; \mathrm{O_2^{\overline{\cdot}}} \longrightarrow -\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2OO^-}}{\underset{|}{\mathrm{CH}}})\!- \;+\; \mathrm{O_2} \qquad (2)$$



$$-\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2OO^-}}{\underset{|}{\mathrm{CH}}})\!- \;+\; -\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2Cl}}{\underset{|}{\mathrm{CH}}})\!- \longrightarrow -\!(\mathrm{O{-}CH_2{-}}\underset{\mathrm{CH_2OO}}{\underset{|}{\mathrm{CH}}})\!- \;\; -\!(\underset{\mathrm{H_2C}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}O})\!- \;+\; \mathrm{Cl^-} \qquad (3)$$

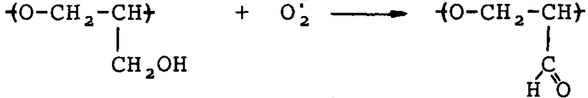
It is known that under such reaction conditions dialkyl peroxides are formed from low molecular weight analogs, thus the proposed mechanism may account for the observed increase in the intrinsic viscosity of PECH in the first stage of reaction. On the other hand, the presence of DMSO allows an efficient cleavage of organic peroxides to the corresponding alcohols, in the case of PECH according to the reaction given below:



$$\underset{\substack{|\\ \text{CH}_2\text{OOH}_2\text{C}\\ \backslash\\ \text{-(CH-CH}_2\text{-O)-}}}{\text{-(O-CH}_2\text{-CH)-}} + 2O_2^{\cdot -} \xrightarrow{(H^+)} \cdot 2\ \underset{\substack{|\\ \text{CH}_2\text{OH}}}{\text{-(O-CH}_2\text{-CH)-}} + 2O_2 \tag{4}$$

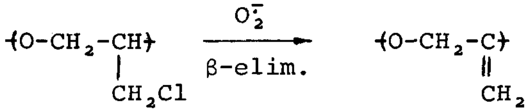
However, attempts to detect the peroxides by chemical methods were unsuccessful, probably because of their low concentration.

A band at ca. 1740 cm^{-1}, assigned to carbonyl absorption, seems to appear as a result of oxidation reactions brought about by superoxide on the hydroxymethyl groups:



$$\underset{\substack{|\\ \text{CH}_2\text{OH}}}{\text{-(O-CH}_2\text{-CH)-}} + O_2^{\cdot -} \longrightarrow \underset{\substack{|\\ \text{C}\\ \text{H}\ \ \text{O}}}{\text{-(O-CH}_2\text{-CH)-}} \tag{5}$$

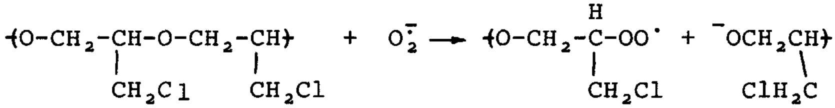
A band at 1640 cm^{-1} assigned to vinylidene absortion presumably appears because of a β-elimination reaction on PECH caused by superoxide:



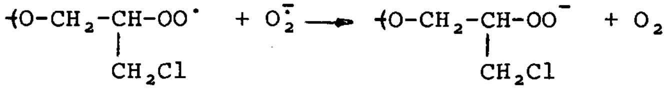
$$\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{-CH)-}} \xrightarrow[\beta\text{-elim.}]{O_2^{\cdot -}} \underset{\substack{\|\\ \text{CH}_2}}{\text{-(O-CH}_2\text{-C)-}} \tag{6}$$

Such a reaction was found to occur on PECH in the presence of potassium hydroxide and sodium methoxide in a number of solvents (NISHIKUBO et al. 1980). It has already been mentioned that superoxide gives elimination products in reactions with alkyl halides.

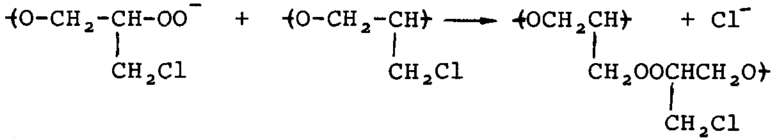
The proposed mechanism of PECH chain degradation by superoxide is as follows: in the first stage superoxide anion attacks an electron-defficient methine carbon atom in PECH backbone:



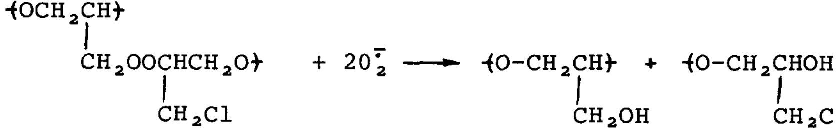
$$\text{-(O-CH}_2\text{-}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{CH}}\text{-O-CH}_2\text{-}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{CH}}\text{)-} + O_2^{\cdot -} \longrightarrow \text{-(O-CH}_2\text{-}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\overset{\text{H}}{\text{C}}}\text{-OO}^{\cdot} + {}^{-}\text{OCH}_2\underset{\substack{\backslash\\ \text{ClH}_2\text{C}}}{\text{CH}}\text{)-} \tag{8}$$



$$\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{-CH-OO}^{\cdot}} + O_2^{\cdot -} \longrightarrow \underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{-CH-OO}^{-}} + O_2 \tag{9}$$

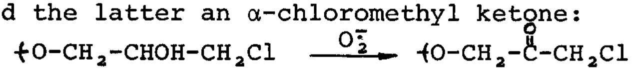


$$\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{-CH-OO}^{-}} + \underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{-CH)-}} \longrightarrow \underset{\substack{|\\ \text{CH}_2\text{OO}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{C}}\text{HCH}_2\text{O)-}}}{\text{-(OCH}_2\text{CH)-}} + \text{Cl}^{-} \tag{10}$$



$$\underset{\substack{|\\ \text{CH}_2\text{OO}\underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{C}}\text{HCH}_2\text{O)-}}}{\text{-(OCH}_2\text{CH)-}} + 2O_2^{\cdot -} \longrightarrow \underset{\substack{|\\ \text{CH}_2\text{OH}}}{\text{-(O-CH}_2\text{CH)-}} + \underset{\substack{|\\ \text{CH}_2\text{Cl}}}{\text{-(O-CH}_2\text{CHOH}} \tag{11}$$

Both kinds of hydroxyl groups formed in reaction 11 may be oxidized, the former giving an aldehyde (reaction 5) and the latter an α-chloromethyl ketone:



$$-\!\!(O-CH_2-CHOH-CH_2Cl \xrightarrow{O_2^{\cdot-}} -\!\!(O-CH_2-\overset{\overset{O}{\|}}{C}-CH_2Cl \qquad (12)$$

The data presented in this communication indicate that solubilized potassium superoxide brings about large changes in the molecular structure of PECH by reacting with the chloromethyl side-groups and by causing a substantial decrease in molecular weight of the polymer. Thus it seems that this reactant cannot be used for the functionalization of linear PECH. It can be employed, however, as a strongly interacting species in various studies concerning polymer degradation, although the varying mode of its action, namely its nucleophilic substitution, reduction, and oxidation properties make it difficult to interpret the results obtained.

Acknowledgement

The author wishes to thank Miss Bożena Cłapka for her technical assistance.

References

DEHMLOW, E. V., and S. S. DEHMLOW, in: "Phase Transfer Catalysis", Verlag Chemie, Weinheim 1980

GIBIAN, M. J., D. T. SAWYER, T. UNDERMANN, R. TANGPOONPHOLVIVAT, M. M. MORRISON J. Am. Chem. Soc. 101, 640 (1979)

JOHNSON, R. A., and E. G. NIDY, J. Org. Chem. 40, 1680 (1975)

NISHIKUBO, T., T. IIZAWA, A. NAKAGAWA, M. OKAWARA, Polym. Prepr., Jpn. 29, 192 (1980)

OSAWA, Z., H. NARANO, E. MITSUI, M. NAKANO, J. Polym. Sci., Polym. Chem. Ed. 17, 139 (1979)

OSAWA, Z., C. MORIYAMA, H. NAKANO, J. Polym. Sci., Polym. Chem. Ed. 19 1977 (1981)

ROBERTS, J. S., Jr. and D. R. SAWYER, J. Am. Chem. Soc. 103, 712 (1981)

SAN FILLIPO, J., Jr., C.-I. CHERN, and J. S. VALENTINE, J. Org. Chem. 40, 1678 (1975)

SAN FILLIPO, J. L., Jr., L. J. ROMANO, C.-I. CHERN, and J. S. VALENTINE, J. Org. Chem. 41, 584 (1976)

SCHACHT, E., D. BAILEY, and O. VOGL, J. Polym Sci., Polym. Chem. Ed., 16, 2343 (1978)

STARKS, C. M., and C. L. LIOTTA, in: "Phase Transfer Catalysis", Academic Press, New York 1978

Accepted December 23, 1981

K