Chlorination and Bromination of Epoxidized Natural Rubber (ENR)

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SYNOPSIS

Epoxidized natural rubber (ENR) with a 25 mol % epoxide content has been chlorinated or brominated in halogenated solvents. The structures of the resulting polymers have been studied by infrared spectrophotometry, and their thermal behavior, by TGA and DSC, and compared with that of chlorinated and brominated natural rubber. For halogenated ENR, a structure of halogenated blocks separated by furanized blocks and products of ring-opening epoxide groups has been proposed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Chlorinated natural rubber (Cl–NR) has found technical application in corrosion-resistant coatings, in paints, and in blends with alkyd resins to impart fire resistance.[1] Recently, a method to epoxidize NR field latex that has been employed also on an industrial scale has been published.[2] We have studied the action of molecular chlorine or bromine on epoxidized natural rubber (ENR) not only to try to understand the structure of the resulting derivatives, but also to study the thermal behavior of Cl–ENR and Br–ENR in comparison with that shown by NR halogenated derivatives (Cl–NR and Br–NR).

EXPERIMENTAL

All solvents and reagents have been the best grades commercially available. NR used for direct chlorination or bromination has been purified as described in Ref. 3.

The epoxidation of NR latex has been carried to 25 mol % as described in Ref. 4, and the epoxide content has been determined by infrared analysis according to a published method.[2] Chlorination of ENR or NR has been performed at room temperature, by bubbling dry molecular chlorine at a rate of about 3.4 g/h into a 1.0% w/v solution of the polymer in dichloromethane. After 2 h of reaction, the product was recovered by precipitation in a large excess of methanol, washed with fresh methanol, and dried in vacuo.

Cl–ENR is a white solid easily soluble in halogenated solvents; from these solutions, transparent films with good adhesion properties to glass, ceramics, and metals can be obtained. Bromination of ENR or NR have been carried on by dropping overnight a dilute solution of bromine in dichloromethane into a 2.0% w/v solution of polymer in carbon tetrachloride, under vigorous stirring to avoid local excess of the halogen. The brominated polymer was recovered by precipitation with methanol, washed, and dried in vacuo. Br–ENR is a gray powder. The infrared spectra have been scanned on films of polymer cast on a NaCl plate from dichloromethane solutions or directly on a thin film of polymer. The infrared spectrophotometer used was a Perkin-Elmer 780 interfaced with a dedicated data station. For thermogravimetric analysis (TGA), use was made of a Perkin-Elmer TGS-2 thermogravimetric system, equipped with a UU1 temperature-control program, a recorder (Perkin-Elmer 56), and a first-derivative computer FDC-1.

The samples were heated at 10°C/min in a nitrogen flow. The differential scanning calorimetry (DSC) of the polymers was performed at 10°C/min under a nitrogen flow on a DSC-30 (Mettler) with the associated TC-10 TA processor.

RESULTS AND DISCUSSION

By controlling temperature it is possible to epoxidize NR with peracetic acid to the desired level of epoxide content, without further reactions and rearrangements.[2,4] NR undergoes epoxidation in a random fashion; at a very low degree of epoxidation, the epoxidized isoprene units are isolated along the polymer backbone, but from about 15 mol % epoxide content, some epoxidized blocks are present and their number increases for a higher degree of modification.[2]

On the other hand, the products of addition of chlorine and NR seem to have complex structures, and only very recently,[3,5,6] it has been shown by infrared and ^{13}C-NMR that the structure of Cl–NR is not exclusively cyclic as proposed previously,[7,8] but mainly linear, even if some cyclization is not completely excluded.[5]

When chlorine or bromine react with ENR, completely new materials are obtained and all the original properties of ENR are lost. The IR spectrum of ENR (Fig. 1) contains two bands characteristic of epoxide rings at 1245 and 870 cm^{-1}. This latter band is used to estimate the epoxide content by
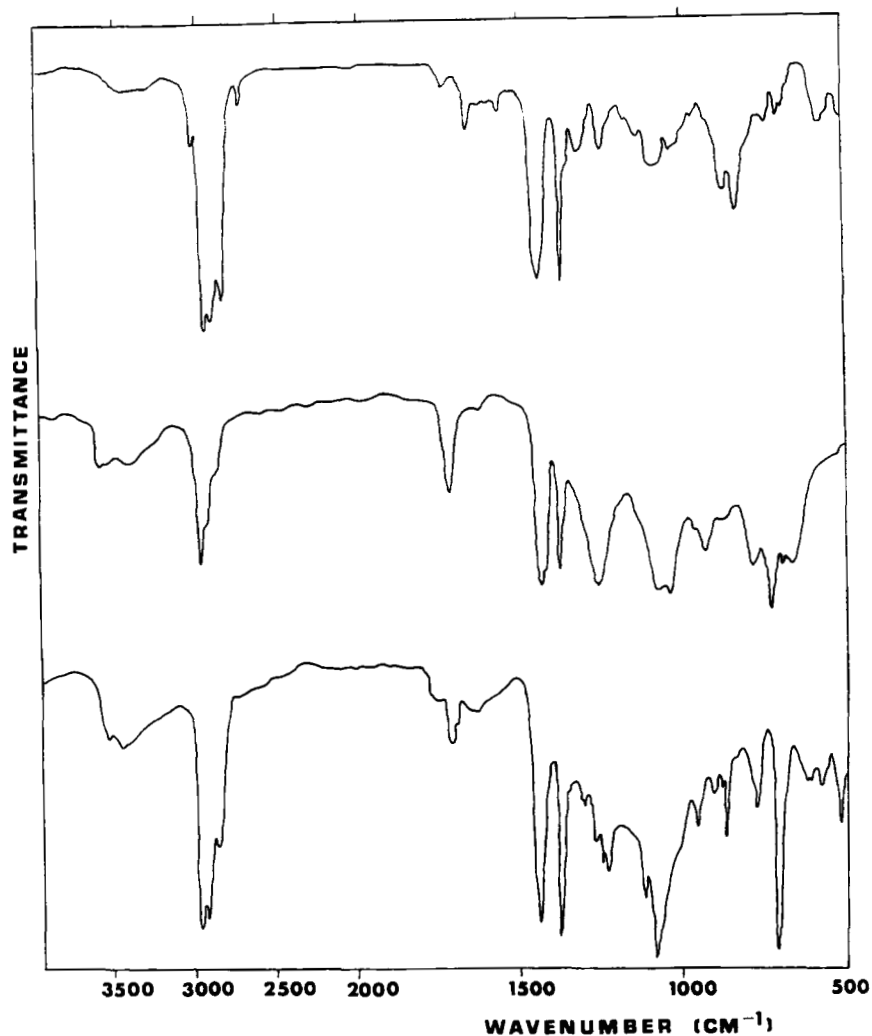
Figure 1   (Top) Infrared spectra of ENR 25 mol %; (middle) of Cl–ENR; (bottom) of Br–ENR.

comparing its absorbance with that at 835 cm^{-1} that is due to residual double bonds.[2] After chlorination of ENR, the epoxide bands disappear with the bands due to the residual olefinic double bonds at 835 cm^{-1}; new bands occur at 3500 and 1720 cm^{-1} due to the ring-opening products of the epoxidized isoprene units, and also a strong band with two minima occurs at 1090 and 1050 cm^{-1} due to cyclic ethers.[2] The band at 1090 cm^{-1} could be due to six-membered cyclic ethers, whereas that at 1050 cm^{-1}, to five-membered cyclic ethers, as has been suggested in studies on model compounds.[2] It is also possible that some cross-link with oxygen bridges could occur. All

the other bands in the IR spectrum of Cl–ENR correspond strictly to those reported by Makani et al.[6] and Hummel[9] for Cl–NR. The IR spectrum of Makani et al. and that of Hummel of course do not show bands at 3500, 1090, and 1050 cm^{-1} that are characteristic of Cl–ENR and also of furanized NR.

ENR reacts with solutions of hydrochloric acid and this reaction can be used to determine its epoxide content.[2] By comparing the data obtained by titration of ENR with hydrochloric acid with data obtained by ^{13}C-NMR on the same sample of ENR, it has been observed[2] that when the epoxide content is below 15 mol % each epoxidized isoprene unit is
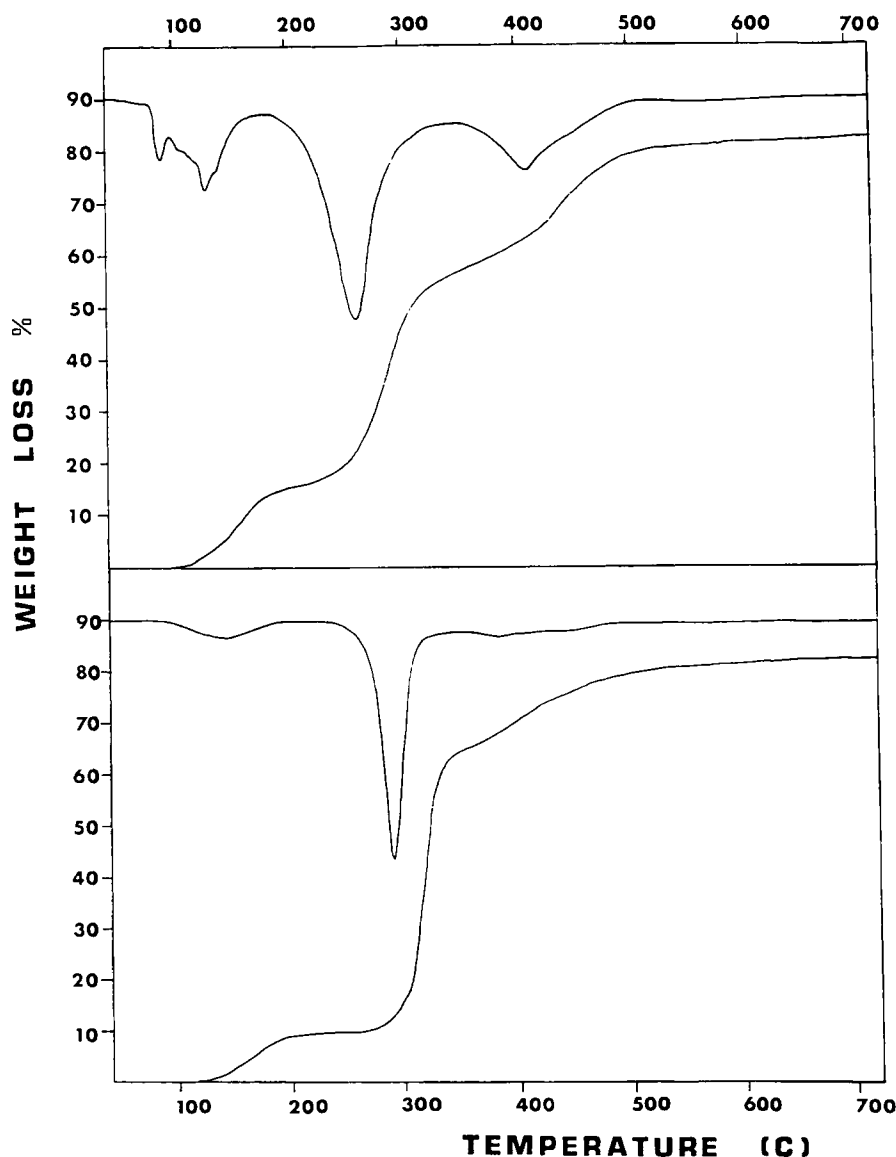

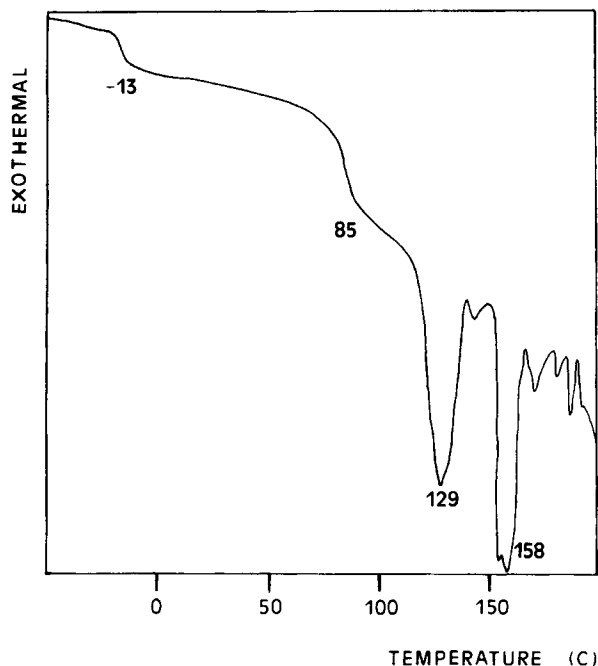**Figure 2**   (Top) TGA and DTA of Cl–ENR; (bottom) Cl–NR.

Figure 3 DSC on Cl-ENR.

isolated in the polymer backbone and reacts with hydrochloric acid to give the chlorohydrin derivative, and the data obtained by titration are in agreement with those obtained by ^{13}C-NMR.

On the other hand, for epoxide content above 15 mol %, the presence of epoxidized blocks along the chain become more probable and is indicated by an increasing discrepancy between the data obtained by titration from those obtained by ^{13}C-NMR. This discrepancy has been interpreted as hydrochloric acid promoting the rearrangement of an epoxidized block to a furanized block. The presence of furanized blocks has been checked by ^{13}C-NMR on titrated samples.[2]

In the early stage of chlorination of NR, hydrochloric acid is evolved.[3] When chlorine attacks an unepoxidized isoprene unit, the hydrochloric acid evolved can possibly promote the ring-opening and the furanization of the epoxidized blocks present along the chain, but chlorine itself could also possibly promote such rearrangement when it attacks a double bond in the proximity of an epoxidized block with the possibility of formation of six- and even seven-membered cyclic ethers or a cross-link.

Bromine attacks the double bonds without the further rearrangements seen for chlorine.[8] The IR spectrum of Br-ENR shows characteristic absorp-

tions at 3500, 1720, and 1085 cm^{-1} and a shoulder at 1050 cm^{-1}, suggesting that essentially the same rearrangements occur in Br-ENR as for Cl-ENR in the epoxidized portions of the chain, whereas the remaining isoprene units undergo simple addition of bromine to the double bonds.

Completely chlorinated NR has the general formula $(C_5H_8Cl_{3.5})_n$.[5,6] From the thermogram for Cl-NR (Fig. 2), decomposition is seen to begin at 138°C and a plateau is reached with a weight loss of about 10%. Assuming that only hydrochloric acid is evolved during this step, it is found that about 0.5 molecules of hydrochloric acid are lost for each chlorinated isoprene unit. At 290°C, the main decomposition begins and a new plateau is reached with a total weight loss of about 75%. This value corresponds strictly to the total chlorine content of Cl-NR plus the chlorinated side methyl groups; in fact $(2.5HCl + CH_2Cl)$ corresponds to 73% by weight of the general formula for Cl-NR already quoted.

Cl-ENR begins to decompose between 90 and 130°C and a plateau is reached with a weight loss of about 18%, probably due to first-stage dechlorination. The main decomposition starts at 260°C with a weight loss in total of about 63%. If Cl-ENR is assigned the general formula

$$\langle (C_5H_8Cl_{3.5})_{0.75n} (C_5H_8O)_{0.25n} \rangle$$
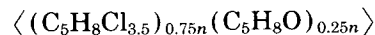
assuming that it is a copolymer of Cl-NR and furanized rubber, 64% weight loss can be expected if the chlorinated portion undergoes decomposition in the same fashion as suggested for Cl-NR.

The DSC on Cl-NR shows a glass transition at 80°C, and an endothermal peak has been detected at 145°C probably due to melting of the polymer with a concomitant decomposition. The complete decomposition occurs at 300°C where a strong exothermal peak has been recorded. Other chlorinated polymers like chlorinated polybutadiene[10] also show glass transitions at about the same temperature as detected here for Cl-NR.

With DSC on Cl-ENR, two distinct endothermic peaks are found (Fig. 3): one at 129°C and the other at 158°C, suggesting that this copolymer has a block-type structure. Moreover, two distinct glass transitions have been detected. The first of these transitions, at −13°C, has been assigned to the furanized portion of the chain, whereas that at 85°C could be due to the chlorinated portion.
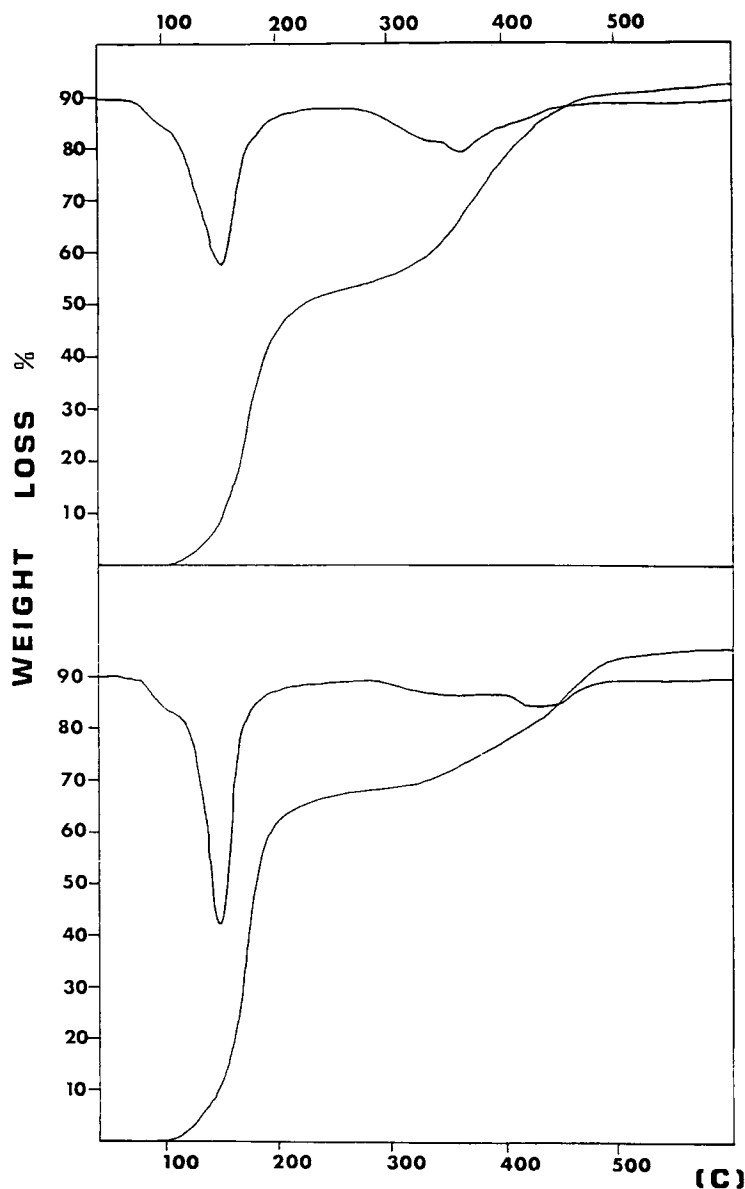
Figure 4   (Top) TGA and DTA of Br–ENR; (bottom) of Br–NR.

TGA on Br–NR (Fig. 4) shows that decomposition starts at 145°C and a plateau with a weight loss of 70% is reached. This weight loss corresponds closely to the theoretical amount of bromine for the general formula $(C_5H_8Br_2)_n$ assigned in the past to Br–NR.[8]

For Br–ENR, decomposition starts at 150°C and a plateau with a weight loss of 60% is reached. Assuming that Br–ENR has the general formula

$$\langle (C_5H_8Br_2)_{0.75n}(C_5H_8O)_{0.25n} \rangle$$
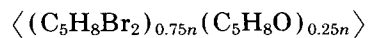
and that it is a copolymer of Br–NR and furanized rubber, weight loss of 62.5% can be expected; this value agrees with the experimental value. DSC on Br–NR shows a glass transition at about 70°C and an endothermal peak at 165°C. For BR–ENR, DSC shows only one glass transition at 30°C and one endothermal peak at 160°C (Fig. 5).
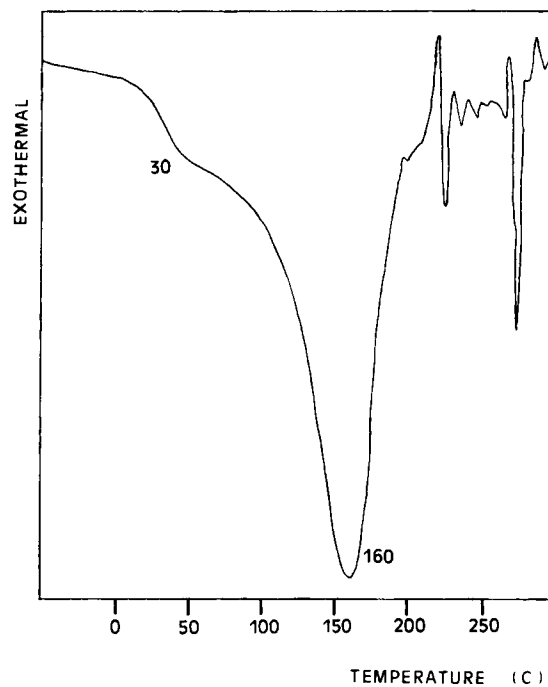
Figure 5   DSC on Br–ENR.

REFERENCES

1. K. J. Saunders, *Organic Polymer Chemistry*, 2nd ed., Chapman and Hall, New York, 1988, pp. 249, 462.
2. A. D. Roberts, *Natural Rubber Science and Technology*, Oxford University Press, New York, 1988, pp. 419–443 and 999–1004 and references therein.
3. L. B. Krentsel, S. O. Travin, A. D. Litmanovic, and K. K. Yutuyan, *Eur. Pol. J.*, **21**, 405 (1985).
4. I. R. Gelling, *Rubber Chem. Technol.*, **58**, 86 (1985).
5. M. V. Eskina, A. S. Khachaturov, L. B. Krentsel, and A. D. Litmanovich, *Eur. Pol. J.*, **26**, 181 (1990).
6. S. Makani, M. Brigodiot, E. Marechal, F. Dawans, and J. P. Durand, *J. Appl. Pol. Sci.*, **29**, 4881 (1984).
7. G. F. Bloomfeld, *J. Chem. Soc.*, 289 (1943).
8. G. F. Bloomfeld, *J. Chem. Soc.*, 120 (1944).
9. D. O. Hummel, *Infrared Spectra of Polymers*, Wiley-Interscience, New York, 1966, p. 107.
10. H. Kawaguchi, Y. Sumida, J. Mugee, and O. Vogl, *Polymer*, **23**, 1805 (1982).