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SPIN TRAPPING REACTIONS WITH NITRIC OXIDES. V. REACTIONS WITH UNSATURATED MACROMOLECULAR CHAINS - A NEW SPIN LABELING METHOD

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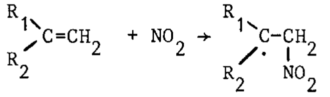
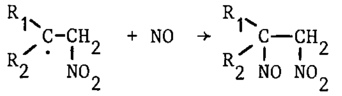
Abstract: Formation of macromolecular nitroxides (i.e., spin labeled polymer chains) has been detected by Electron Spin Resonance spectroscopy in the reaction of nitric oxide gas with several unsaturated polymers /synthetic polyisoprene, polybutadiene, poly(isoprene-co-isobutylene), poly(butadiene-co-styrene)/ dissolved in aromatic hydrocarbons. Spectroscopic evidences of gel formation, precipitation, and of solvent effect have been given.

In the course of our continued investigations concerning the reactions of nitric oxide with free radicals and olefins we have shown that stable nitroxyl radicals are produced from unsaturated compounds via pseudonitrosite, if trace amount of NO_2 is present[1]:

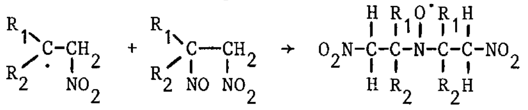


(1)



pseudonitrosite

(2)

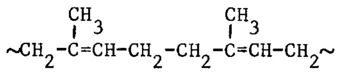


(3)

This set of consecutive radical reactions gave us the idea to introduce nitroxyl functionality into polymer chains containing main-chain and/or side-chain double bonds.

Earlier studies of Bloomfield and Jeffrey[2] have shown that the reaction of nitric oxide with rubber and its model compounds represents characteristics of a free-radical reaction, the precise mechanism of which was considered to be obscure. However, in the cited paper there is no mention made of nitroxyl radicals, although they stated that the model compounds yielded "products which appeared to contain substituent nitro-groups, together with substances of rather lower oxygen:nitrogen ratio."

In our experiments we have selected some of the most common rubber polymers, i.e., homo- and copolymers of isoprene and butadiene, such as

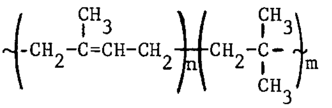


$$\sim CH_2\text{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}\text{=}CH\text{-}CH_2\sim$$

polyisoprene

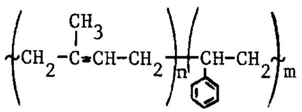
$$\sim CH_2\text{-}CH\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH\text{=}CH\text{-}CH_2\sim$$

polybutadiene



$$\left(\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}\text{=}CH\text{-}CH_2\text{-}\right)_n\left(\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{-}\right)_m$$

poly(isoprene-co-isobutylene)

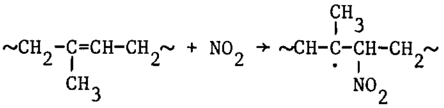


poly(butadiene-co-styrene)

Synthetic polyisoprene (Shell, $\overline{M}_n = 6\cdot10^4$, 96 % cis), polybutadiene (Ameripol CB-220, $\overline{M}_n = 1.3\cdot10^5$, 98 % cis), poly(isoprene-co-isobutylene) (BF Goodrich, $\overline{M}_n = 2.3\cdot10^5$, 2.5 % isoprene content), and poly(butadiene-co-styrene) (Firestone FRS 206, $\overline{M}_n = 4.1\cdot10^3$, styrene content 23 - 29 %) were purified repeatedly by dissolving in benzene then precipitating with methanol, followed by drying.

Introduction of NO gas into the ESR sample tube that contained benzene solutions of these polymers gave rise to macromolecular nitroxides. The rate of formation increased with increasing concentration of oxygen remained in the solution after deaerating with argon. The NO formation and sample deaeration procedures as well as the ESR apparatus (JEOL-JES-FE-3X) were the same as described earlier[3].

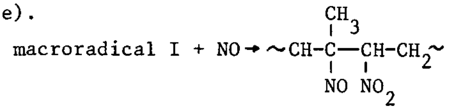
In the case of the isoprene polymers the reaction sequence that leads to nitroxides is supposed to proceed on the analogy of reactions (1)-(3).



$$\sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2\sim + NO_2 \rightarrow \sim CH-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-\underset{NO_2}{\underset{|}{CH}}-CH_2\sim \qquad (4)$$

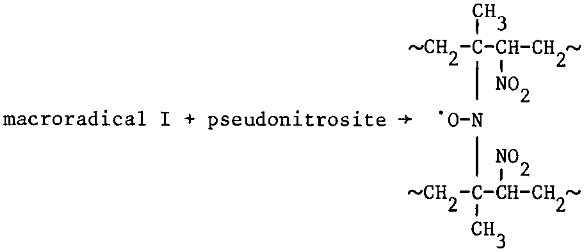
macroradical I

Radical trapping of macroradical I by NO yields a macromolecular nitroso-nitro compound (pseudonitrosite).



$$\text{macroradical I} + NO \rightarrow \sim CH-\overset{CH_3}{\overset{|}{\underset{NO}{\underset{|}{C}}}}—\underset{NO_2}{\underset{|}{CH}}-CH_2\sim \qquad (5)$$

The presudonitrosite can be considered as a sensitive spin-trapping agent that reacts with any C-radical. Depending on whether this radical site is on the same chain or on another, radical trapping can proceed either in intramolecular or intermolecular way, which leads to cyclization or crosslinking, respectively.



$$\text{macroradical I} + \text{pseudonitrosite} \rightarrow \begin{array}{c} \sim CH_2-\overset{CH_3}{\overset{|}{C}}-\underset{NO_2}{\underset{|}{CH}}-CH_2\sim \\ | \\ {}^{\bullet}O-N \\ | \\ \sim CH_2-\underset{CH_3}{\underset{|}{C}}-\overset{NO_2}{\overset{|}{CH}}-CH_2\sim \end{array} \qquad (6)$$

The lack of resolved β-H splitting in the case of butadiene polymers (Fig.1.b,d) can be explained either by a strongly hindered conformation due to the polymer chain, which leads to a strongly reduced β-H hyperfine coupling constant, or by the transformation of secondary alkyl radical formed from the addition of olefin and NO_2 into a tertiary radical.

The ESR spectra shown in Figures 1 and 2 provide evidence in support of the assumed mechanism. As it can be seen in Fig.1, the four different diene homo- and copolymers give rather similar spectra consisting of three ^{14}N hyperfine lines of different line width, which is characteristic of large-size elongated nitroxyl radicals undergoing slow rotational reorientation in isotropic liquid media[4,5,6,7]. All these spectra refer to dissolved macromolecular chains (sol phase) with $>N-O^{\bullet}$ moiety attached covalently to the backbone. The spectral paramters are the following: (a) g value = 2.0059, $a_N = 1.528$ mT; (b) g value = 2.0060, $a_N = 1.542$ mT; (c) g value =

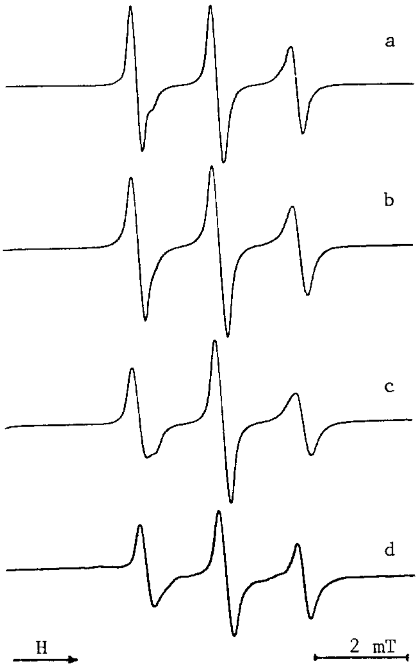


Figure 1: ESR spectra of nitroxides formed in toluene solution of diene polymers treated with nitric oxide.

a: polyisoprene
b: polybutadiene
c: poly(isoprene-co-isobutylene)
d: poly(butadiene-co-styrene)
Concentration: 2 w%

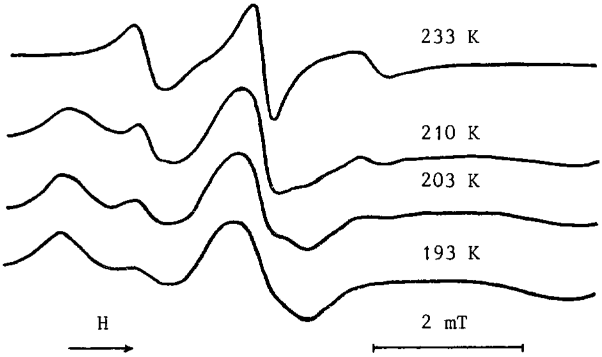


Figure 3: ESR spectra of 2 w% toluene solution of poly(isoprene-co-isobutylene) at different temperatures.

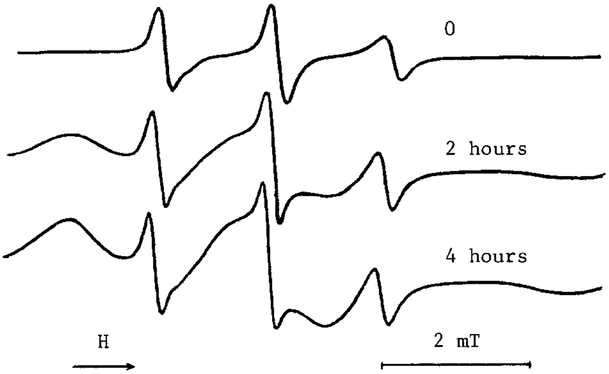


Figure 2: Gel formation in 5 w% toluene solution of polyisoprene treated with NO as monitored by recording room temperature ESR spectra. The time elapsed after NO gas admission is shown above the spectra.

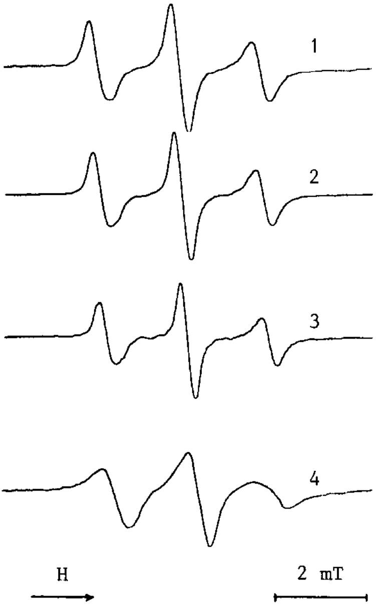


Figure 4: Room temperature ESR spectra of spin labeled poly(isoprene-co-isobutylene) dissolved in toluene/acetone mixtures. Toluene/acetone volume ratios 1:30/1, 2:30/2, 3:3/1, 4:3/2.

2.0063, $a_N = 1.514$ mT; (d) g value = 2.0059, $a_N = 1.432$ mT, (room temperature data).

Gelation starts quite early in the case of the two homopolymers, i.e., polyisoprene and polybutadiene. That means increasing number of double bonds along the polymer chain leads to higher probability of intermolecular radical trapping visualized by reaction (6). This process can be monitored by recording ESR spectra at different time intervals after nitric oxide admission into the samples. Figure 2 shows the build-up of the superimposing asymmetric broad triplet spectrum assigned to polymer nitroxides that undergo strongly hindered molecular motion due to the gel phase.

In order to substantiate our supposition that the nitroxides formed are of macromolecular character, other ESR spectroscopic evidences have been gathered by studying temperature and solvent effects on chain mobility. For this purpose we selected the toluene solution of poly (isoprene-co-isobutylene) treated with nitric oxide.

Decreasing the temperature of the test solution resulted in reduced solubility of the labeled polymer. Visual inspection showed that at about 220 K the solvent became hazy. Simultaneously, a broad "solid" signal appeared and then became predominant in the spectrum (Fig.3), showing that the precipitation process was going on. On warming back to room temperature we obtained the original spectrum again, i.e., the precipitation and the corresponding spectral changes seem to be reversible.

Another simple experiment has shown that the continuous change of solvent composition affects markedly the molecular mobility of the labeled polymer chain, if the added component is a precipitator. In the present case acetone was added in very small portions to the toluene solution of poly(isoprene-co-isobutylene). As can be seen in Fig.4., at higher acetone content the three-line ESR signal becomes more asymmetric, which means that the reorientation frequency of tumbling macronitroxides decreases.

Similar spectra were obtained with natural rubber dissolved in toluene, and also with pure oleic acid, a short-chain model compound of unsaturated polymer chains.

References

1. A.Rockenbauer, M.Győr and F.Tüdős: submitted for publication to Tetrahedron Letters
2. G.F.Bloomfield and G.A.Jeffrey: J.Chem.Soc., 120 (1944)
3. M.Győr, A.Rockenbauer and F.Tüdős: submitted for publication to Tetrahedron Letters
4. J.H.Freed: in Spin Labeling, Theory and Application, Ed. L.J.Berliner, Academic Press, New York, 1976, Vol.I. pp 53-132
5. R.F.Boyer and S.E.Keinath, Ed. "Molecular Motion in Polymers by ESR"; Harwood Academic Press, New York, 1978, MMI Press Symposium Series, Vol. 1
6. J.S.Hwang and C.P.Tsonis: Macromolecules, 16, 736 (1983)
7. M.Shiotani, J.Sohma and J.H.Freed: Ibid., 16, 1495 (1983)

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