^{13}C-NMR Evidence for Hydrogen Supply by Water for Polymer Cracking in Supercritical Water

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(Received October 18, 1996)

A rubber polymer (EPDM, ethylene-propylene-diene-terpolymer) vulcanized was cracked to paraffinic oil (PO) in NaOH-containing supercritical water (SCW) at 420 °C and 30 MPa. The SCW polymer cracking is not oxidative but reductive. The ^{13}C-NMR analysis of PO obtained by SCW D_2O cracking demonstrates that the terminal methyl carbons are deuterated as a clear indication of hydrogen supply by SCW in the cracking.

To keep clean our earth environment, it is a promising project to crack and wash the sulfur-cured (vulcanized) EPDM rubber to obtain useful PO through a reductive SCW reaction and to elucidate the mechanism by applying modern NMR spectroscopy. Recently, SCW oxidative decomposition of hazardous compounds has been explored as a new treatment method for compounds containing halogen atoms.[1-3] The oxidative method leads to the thorough depletion of C-H and C-C bonds and the unavoidable emission of CO_2 as a source of the green house effect. The drawback urges us to study the SCW reductive cracking of polymers. If we can find a reaction pathway where such wasted and nuisance materials are transformed into a useful form between polymeric and monomeric ones, the CO_2 emission to the atmosphere is reduced and delayed because C-H and C-C bonds can be regained and retained, respectively.

The rubber investigated was synthesized by adding fillers (carbon black and paraffin) and curatives (zinc oxide, sulfur, etc.) to an EPDM polymer containing ENB (2-ethylidene-5-norbornene) as a diene monomer. The EPDM polymer used in this study has a large molecular weight (weight average, 500000), consisting of ethylene (68 mol%), propylene (29 mol%), and ENB (3 mol%). The rubber components are: EPDM (100), carbon black (80), paraffinic softener (60), zinc oxide (5), stearic acid (2), sulfur (2), and dibenzothiazyl disulfide (2); the parenthesized numbers are the relative compositions by weight.

In the SCW cracking, the rubber of 3.8 g was mixed with water (H_2O or D_2O) containing 1 mol/dm^3 NaOH in a degassed and argon-filled vessel (42 cm^3) made of Hastelloy-C276. The temperature and pressure inside the vessel were monitored directly. The SCW reaction products in the liquid phase were washed with water and hexane. The oil phase has been separated from the aqueous one by hexane and dried. The rubber is cracked into PO at 420 °C where PO and the initial paraffin are almost identical with respect to molecular weight (MW) of ~1000. The yield, which is defined by the weight ratio of PO to the sum of the EPDM and the paraffin softener, amounts to ~0.9 at this optimum temperature; most of the remainder is dissolved and lost in water. This exceeds the formal ratio of 60/160 = ~0.38 for the paraffin contained in the rubber before the cracking. A large fraction of PO is produced by the rubber cracking. PO with a low residual sulfur content of <0.1% (w/w) enables us to recycle the PO thus obtained. Without NaOH the sulfur content was one order of magnitude higher, and such contaminated PO could not be reused for producing quality rubber.

To directly prove structural changes accompanying the SCW cracking, we have performed ^{13}C-NMR analysis. Figure 1 shows that the ^{13}C spectra of the EPDM polymer, PO, vulcanized EPDM rubber, and paraffin softener in the region of saturated carbons, such as CH_3, CH_2, and CH. To find spectral correlations, we compare these four spectra. Correlations are indicated by the vertical lines tying the carbon peaks common to

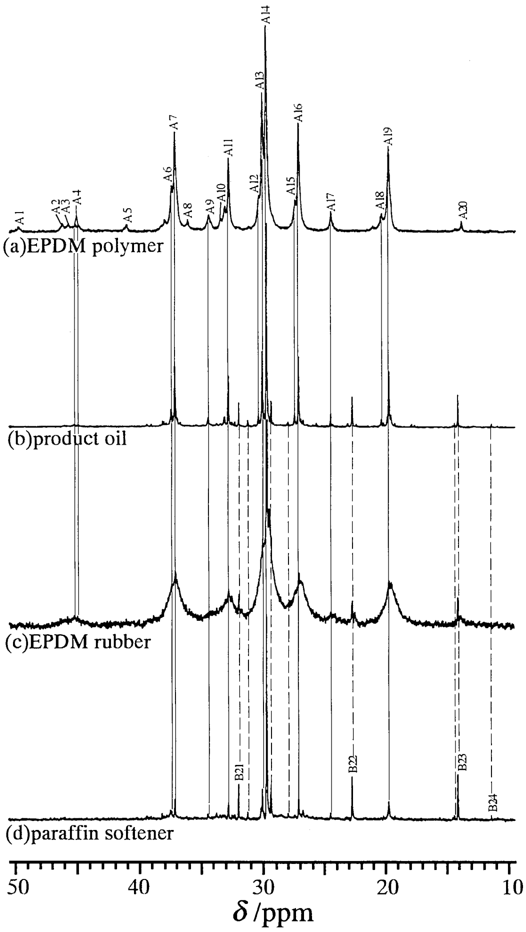

Figure 1. Correlated ^{13}C spectra of PO obtained by SCW cracking of the rubber and the relevant compounds at 30 °C. δ denotes the chemical shift (ppm) relative to TMS. (a), EPDM polymer (swollen in $CDCl_3$), (b) PO (neat), (c) vulcanized rubber (swollen in $CDCl_3$), and (d) softener paraffin (neat). A NMR spectrometer (JEOL, EX270) was operated at 67.80 MHz.

the relevant compounds. The strong peaks observed for PO arise from the previously assigned[4,5] peaks (A4, A6, A7, A9, A11-19) in the EPDM polymer. Then see the solid lines. The remaining strong peaks come from the peaks (B21-24) of branched carbon atoms[6] present in the softener paraffin. Next see the broken lines. Although the segmental motion restriction due to the sulfur-induced cross-linkages between the polymer chains leads to such a low resolution of the vulcanized rubber, we can see that most of the strong and broad peaks are shared by the rubber and EPDM polymer, and that the strong and sharp peaks are shared by the rubber and the paraffin softener. No carbons attached to an oxygen atom were detected in the lower magnetic field; this is true also in the case of ^{1}H. The absence of peaks at the low field as well as the insolubility in water indicates that the SCW cracking is not oxidative.

Furthermore, it is to be noted that the peaks A1-3, A5, A8, A10, and A20, which are assigned[5] to the carbons of ENB contained in the EPDM polymer, are all lost in the spectrum of PO; ENB (3 mol%) is incorporated into the polymer in order to make the rubber elastic through cross-linkages formed by vulcanization. The loss indicates that the cracking is associated with the SCW detachment of the cross-linkages. Cross-linking bonds, which are minor in abundance but major in function in rubbers, are selectively broken by the fairly mild reactivity of SCW; sulfurs are likely to be transformed into water-soluble forms. It is to be noted that the EPDM polymer itself was reductively cracked by SCW without the fillers nor curatives. This suggests that a key role in controlling the cracking is played not by sulfur but by ENB.

We now focus on the unassigned new peaks in Figure 1(b) because only these carry on key information on the mechanism of the SCW reductive cracking. New peaks of PO are all weak because the number of terminal carbon atoms created must be much smaller in view of the MW of ~1000. The relative intensity of the new peaks increases with increasing degree of the cracking. In Figure 2, the ^{13}C spectrum of the PO produced by SCW D_2O reaction at 420 °C and 35 MPa for 120 min is compared with that of the PO produced by SCW H_2O reaction at 420 °C and 30 MPa for 30 min. To unveil hidden weak peaks among strong ones, the spectra are largely expanded only vertically, and thus most of the strong peaks referred to above are scaled out.

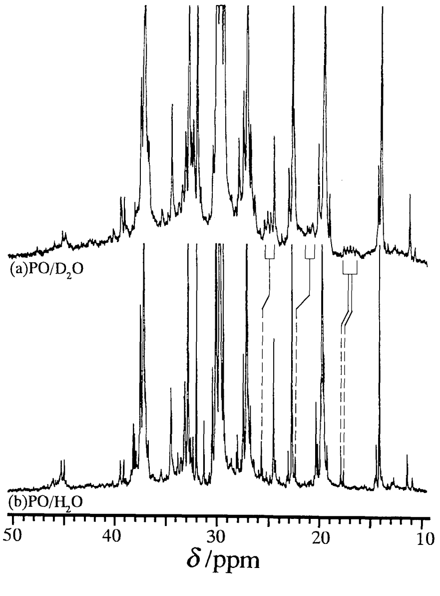

Figure 2. Correlation of the ^{13}C spectra at 30 °C of the oils obtained from the SCW cracking in H_2O and D_2O. (a)PO/D_2O, the PO generated by SCW D_2O cracking at 420 °C and 35 MPa for 120 min, and (b)PO/H_2O, the PO generated by the SCW H_2O cracking at 420 °C and 30 MPa for 30 min. Carbons at $\delta < 27$ ppm are methyl carbons according to DEPT (Distortionless Enhancement by Polarization Transfer) measurements.

We anticipate that if the SCW cracking is reductive as above-mentioned, some of the weak peaks assignable to the end carbons generated by cracking are to be influenced by the addition of D supplied by SCW D_2O. As can be seen in Figure 2, at least four CH_3 carbons at 25.7, 22.4, 17.9, and 17.7 ppm shift by ~1 ppm to a higher field and show a multiple splitting due to ^{13}C-^{2}H coupling[7] as a result of the ^{2}H incorporation into the chain ends; the triplet splitting suggests a form of CH_2D. The evidence for the direct attachment of D to the terminal methyl carbons confirms the SCW hydrogen supply mechanism for the breakage of carbon-carbon bonds. This has been also proved by the comparison of the ^{2}H spectra corresponding to (a) and (b) in Figure 2; the intensity measurement of ^{2}H in the methyl region has led to determination of the ^{2}H concentration in the order of 10^{-3} mol/g. This is in reasonable agreement with the approximate MW value of 1000 for PO. Cheap supply of useful hydrogen from SCW is of great importance.

To support the reaction mechanism, it is important to analyze the product gases by gas chromatography. The total gas yield was ~1% (w/w) relative to the total weight of the initial EPDM and paraffin. The components and compositions are:

$$H_2(65\%) > N_2(22\%) > CH_4(3\%) > C_2H_6(2\%)$$
$$= C_3H_6(2\%) = C_3H_8(2\%) > n\text{-}C_4H_{10}(1\%)$$

where the parenthesized numbers indicate the volume % of the gases under the normal conditions. A large amount of hydrogen is generated, and neither CO_2 nor CO are detected. The excessive hydrogen in the gaseous mixture supports that the SCW cracking proceeds under reductive conditions. This is in agreement with the microscopic findings based on the ^{13}C-NMR analysis of PO. H_2O is formed by a catalytic, photochemical or photoelectrochemical reaction between H_2 and O_2. Although the reaction is highly irreversible under usual conditions, we can regard SCW at high enough temperatures as a supplier of hydrogen and oxygen atoms in SCW material transformations.

References and Notes

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