Study of thermal degradation of polybutadiene in inert atmosphere: 2. Characterization of thermal crosslinking in polybutadiene by high resolution solid state ^{13}C and ^{1}H magic angle spinning n.m.r. spectroscopy

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The chemical structure of polybutadiene thermally crosslinked at temperatures up to 250°C was characterized by high resolution solid state ^{13}C n.m.r. spectra in combination with high resolution ^{1}H and ^{13}C magic angle spinning n.m.r. spectra of the swollen gel. Crosslinking is shown to involve the reaction of a vinyl group with the methylene group in 1,4-*cis*/1,2 sequences.

(Keywords: ^{13}C CP/MAS; ^{1}H MAS n.m.r.; polybutadiene; thermal crosslinking)

Introduction

Thermal degradation of polybutadiene (PB) has been the subject of numerous studies[1] (and references cited therein). It is generally agreed that at temperatures up to 250°C, the main process is crosslinking. By heating to 300°C and above, this crosslinked polymer is decomposed yielding soluble degradation products[1]. The structure of the crosslinked product was studied by i.r. spectroscopy, but only the extractables have been studied by n.m.r. methods so far. Both i.r. and n.m.r. evidence was obtained for the saturation–cyclization process[2], based on the appearance of the methyl peak at 1373 cm^{-1} in i.r. spectra and at 0.9 ppm in ^{1}H n.m.r. spectra, together with peaks at 1.55 and 1.25 ppm assigned to secondary and tertiary hydrogen on saturated carbon atoms, presumably in condensed rings. Considering kinetic data and the low activation energy of the process, non-radical crosslinking was proposed by Grassie and Heaney[3], consisting of the addition of a reactive vinyl group to a methylene group of 1,4-PB activated by a neighbouring double bond. This mechanism would leave the original *cis*- and *trans*-1,4 structures practically unchanged. Recently, ^{13}C n.m.r. spectroscopy was applied to the analysis of photo-oxidized and peroxide-crosslinked PB[4], using noise decoupled spectra for lightly crosslinked swollen material, and magic angle spinning (MAS) n.m.r. with high-power dipolar decoupling for the more strongly crosslinked samples. For the former case, two crosslinking mechanisms are proposed, but for the latter case, the experimental evidence was found to be inconclusive.

Obtaining data on the relative amounts of various chemical groups by solid state high resolution ^{13}C n.m.r. methods is never straightforward. In chemically crosslinked polymer networks, the difficulties would be amplified by a possible non-homogeneous distribution of crosslink points, therefore any additional information would be welcomed. In elucidating the chemical structure of linear polymers in solution, the combination of ^{1}H and ^{13}C n.m.r. spectroscopy has proved to be most useful. In our previous work[5–7] it has been shown that high resolution ^{1}H n.m.r. spectra of crosslinked polymers that swell to some extent in a suitable solvent can be obtained by measurement with MAS at frequencies of several kilohertz. Therefore in the present work, as part of a broader study of thermal degradation of PB[1], we have attempted to apply solid state ^{13}C n.m.r. methods (using MAS and high-power dipolar decoupling with or without cross-polarization) in combination with ^{1}H MAS n.m.r. to investigate the chemical nature of the thermally crosslinked PB network.

Experimental

The materials studied were the same as the solid samples 200/4S and 250/2S of part 1 of this work[1], prepared by heating a PB rubber containing 34% of *cis*-1,4-PB, 54% of *trans*-1,4-PB and 11% of 1,2-PB units in inert atmosphere to 200°C for 4 h and to 250°C for 2 h, respectively. For measuring n.m.r. spectra, the original PB rubber was dissolved and the insoluble products of thermal treatment were swollen to equilibrium in $CDCl_3$, with hexamethyldisiloxane (HMDS) as internal standard ($\delta = 0.05$ ppm in ^{1}H and 2 ppm in ^{13}C).

Conventional high resolution ^{1}H and ^{13}C n.m.r. spectra were measured with a Bruker spectrometer (model AC 300) at 300 and 75 MHz, respectively, at ambient temperature. N.m.r. spectra of the solid samples and of the swollen gels were measured with a Bruker spectrometer (model MSL 200), at 200 MHz for ^{1}H and 50 MHz for ^{13}C, using solid state high resolution n.m.r. methods. Dry samples were packed in standard double-bearing rotors, while for swollen gels and the solution of original PB, KEL-F rotors of our own construction were used[8]. ^{1}H spectra were measured with the MAS technique. ^{13}C spectra were measured both with cross polarization (CP)/MAS, i.e. the standard combination of CP, MAS and high-power proton dipolar decoupling[9], and without CP, i.e. using single pulse excitation together with MAS and high-power proton dipolar decoupling. A MAS frequency of ~3 kHz was used in all measurements.

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Results and discussion

^1H n.m.r. The conventionally measured high resolution ^1H n.m.r. spectrum of the PB sample 200/4S, swollen to equilibrium in $CDCl_3$, is shown in *Figure 1a*. It exhibits bands with relatively sharp peaks but extremely broad wings of so-called super-Lorentzian shape[5,10]; by MAS, these lines could be reduced to Lorentzian shape, of widths comparable to those of the original polymer in solution (*Figure 1b*). ^1H n.m.r. lines of super-Lorentzian shape and susceptible to narrowing by MAS are usually observed in systems with relatively rapid internal motions that are anisotropic in space, with residual near-static dipolar interactions[5]. Typical examples of such systems are liquid crystals[10–12], and swollen crosslinked polymer gels[6,7]. Thus the high resolution ^1H n.m.r. spectra of sample 200/4S swollen to equilibrium in $CDCl_3$, measured with and without MAS, confirm that the main effect caused by heating at 200°C is crosslinking, as previously suggested.

Sample 250/2S swells much less than sample 200/4S in $CDCl_3$. A conventionally measured ^1H n.m.r. spectrum of sample 250/2S swollen to equilibrium in excess $CDCl_3$ shows linewidths much too broad to reveal any information on chemical structure. Nevertheless, a well-resolved ^1H n.m.r. spectrum of this sample, suitable for chemical analysis, can be obtained with ^1H MAS n.m.r. (*Figure 2b*); this spectrum is compared with a similarly measured spectrum of the original PB in $CDCl_3$ solution (*Figure 2a*). With the crosslinked sample 250/2S, the linewidth thus measured for 1,4 and 1,2 structures is only about 1.5 times broader than that of the linear polymer. The relative intensity of the bands of 1,2 structures around 4.9 ppm is somewhat reduced, while many overlapping bands appear in the aliphatic region. Of these, the most prominent are the methyl peak at $\delta = 0.85$ ppm, the very sharp peak at $\delta = 1.25$ ppm (both these peaks are thought to be connected with the saturation–cyclization process[2] and they remain prominent in the soluble products of heating to higher temperatures[1]) and the peak at $\delta = 2.75$ ppm which could be assigned to CH groups α to a double bond with a *cis* substituent, or surrounded by highly branched structures[13]. Nevertheless, the ^1H n.m.r. spectrum of the crosslinked PB sample 250/2S is still dominated by absorption of 1,4-PB, with an olefinic: aliphatic proton ratio of ~1:2, indicating that the content of chemically changed structures, and of structures connected with the crosslinking process, is low.

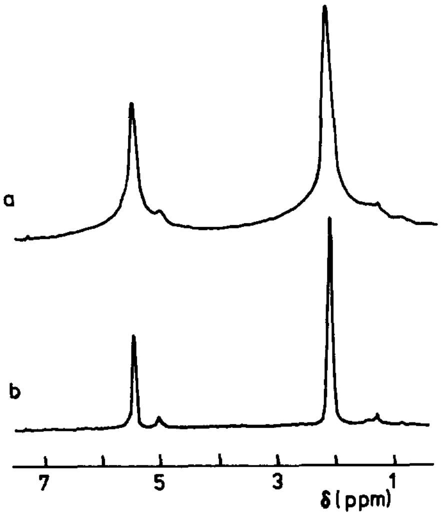


Figure 1 ^1H n.m.r. spectra of thermally treated PB sample 200/4S swollen to equilibrium in $CDCl_3$ with HMDS: (a) measured conventionally at 300 MHz (spectral width 6 kHz, 30° pulse, pulse repetition time 2.7 s, 64 scans); (b) measured with MAS at 200 MHz (spinning frequency 2750 Hz, spectral width 2 kHz, 90° pulse, pulse repetition time 5 s, 256 scans)

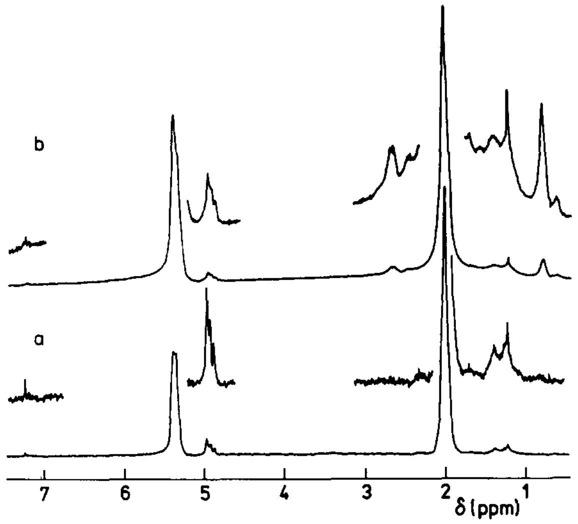


Figure 2 200 MHz MAS ^1H n.m.r. spectra of (a) original PB (10% w/v in $CDCl_3$ with HMDS); (b) thermally degraded sample 250/2S swollen to equilibrium in $CDCl_3$. Spinning frequency 2750 Hz, spectral width 2 kHz, 90° pulse, pulse repetition time 5 s

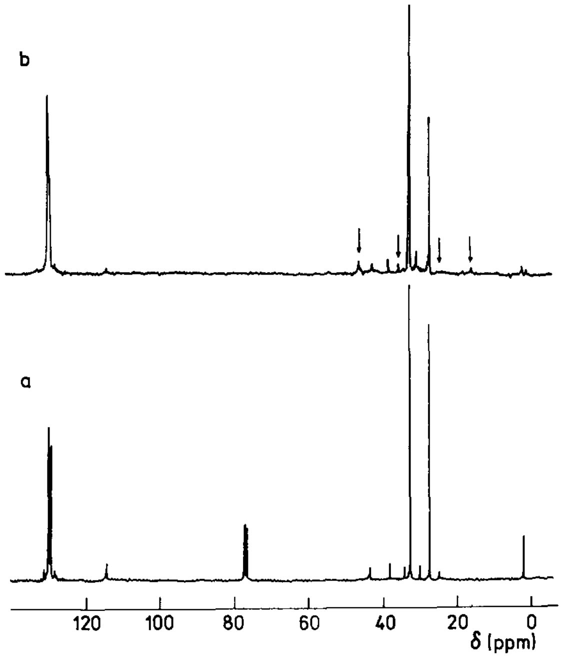


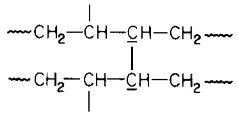
Figure 3 ^{13}C n.m.r. spectra of (a) original PB (10% w/v in $CDCl_3$ with HMDS), conventional liquid state 75 MHz high resolution spectrum (spectral width 25 kHz, 30° pulse, pulse repetition time 1.67 s, 1000 scans); (b) thermally degraded sample 250/2S (swollen to equilibrium in $CDCl_3$); 50 MHz CP/MAS spectrum (spinning frequency 2840 Hz, contact time 5 ms, decoupling power in frequency units 60 kHz, pulse repetition time 6 s, 2840 scans). Newly appearing, or disappearing, peaks are marked by arrows

^{13}C n.m.r. In *Figure 3*, the conventionally measured (with low-power noise decoupling) high resolution ^{13}C n.m.r. spectrum of the original PB in $CDCl_3$ solution is compared with the ^{13}C n.m.r. spectrum of sample 250/2S

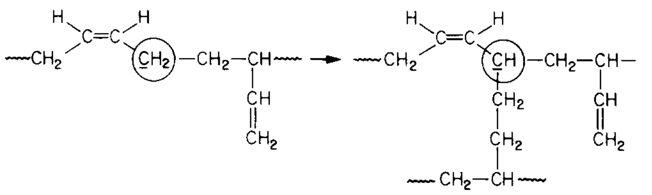
swollen in $CDCl_3$ measured by the CP/MAS n.m.r. technique. Essentially the same spectra were obtained when the sample 250/2S was measured in the swollen state by ^{13}C MAS n.m.r. without CP, or when it was measured in the dry state by the same two procedures. These experiments were necessary because measurements with CP usually favour the detection of structures with near-static dipolar interactions, whereas MAS n.m.r. with high-power decoupling without CP also reveals the material containing more mobile segments, with rapid isotropic internal motion. Any difference between the above types of measurement would reveal the presence of phases which differ both in their motional characteristics and in chemical structure. The observed lack of difference indicates that the conclusions on chemical structure drawn from the spectra in *Figure 3* should be valid for the whole mass of the studied sample.

The two spectra in *Figure 3* are very similar: in the spectrum of the heat-treated sample only weak new peaks appear in the methyl group range at 16 ppm, and at 36 and 47 ppm in the range of aliphatic carbons in unsaturated structures; the weak peak at 25 ppm of the original spectrum has disappeared after heat treatment.

The peak at 36 ppm agrees with the frequency assigned[4] to branched structures of the type:



The weak peaks in the range 20–45 ppm have been assigned[14–16] to CH_2 groups in various sequences containing 1,2 structures. The 'lost' peak at 25 ppm has been assigned to the CH_2 group in a 1,4-*cis*/1,2 sequence.



Addition of a vinyl group at this carbon could be regarded as a specific case of the Heaney–Grassie mechanism[3]. It is compatible with the appearance of the peak at 2.7 ppm in the ^1H n.m.r. spectrum. Assignment of the ^{13}C n.m.r. peak at 47 ppm to the carbon atom at this specific crosslink point can only be speculative at present. The ^1H n.m.r. peak at 2.7 ppm disappears in the (soluble) products of heating to higher temperatures[1], indicating that the neighbourhood of the respective group is preferentially susceptible to cleavage.

Conclusion

Measurements of ^1H MAS n.m.r., together with ^{13}C n.m.r. spectra, confirm the occurrence of the previously proposed non-radical crosslinking mechanism in thermal degradation of PB. These results indicate that in attempts to elucidate the chemical nature of crosslinking in polymer networks, high resolution ^1H MAS n.m.r. of the swollen gel can provide additional evidence, complementing that obtained by i.r. and solid state high resolution ^{13}C n.m.r. methods.

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