^{13}C CP/MAS NMR Study of the Inclusion Polymerization of 2,3-Dimethylbutadiene in Deoxycholic Acid

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ABSTRACT: Stages of the polymerization process of 2,3-dimethylbutadiene (DMB) included in deoxycholic acid (DCA) have been studied by ^{13}C CP/MAS NMR spectroscopy. The spectra show the monomer complex bis(deoxycholic acid)/(2,3-dimethylbutadiene) to have two crystallographically distinct DCA molecules in the structure. Spectral broadening in the dipolar decoupling regime indicates the occurrence of at least two dynamic processes of the included DMB molecules, with rates on the order of 10^5 Hz in the temperature region of 219–336 K. The dynamic processes have been linked to the observed features of postirradiative polymerization. ^{13}C CP/MAS NMR spectra of the DCA inclusion complex after postirradiative polymerization show polymer formation in ca. 66% yield. This polymer was also studied after isolation. The spectral differences in the two cases are interpreted in terms of effects due to the local environment of the alkene carbons.

Introduction

"Inclusion polymerization" is the phenomenon whereby monomeric species present in channel-type inclusion complexes may be induced to undergo polymerization by high-energy radiation (β-, γ-, or X-rays).[1] It appears that the scope of inclusion polymerization is limited by substrate specificity in a similar manner to many template reactions. Inclusion polymerization is capable of being highly selective at both constitutional and stereochemical levels,[2] presumably due to spatial constraints on, and controlled relative orientations of, the monomers within the inclusion environment. The differences in the constitutional and steric regularity of the resultant polymers observed amongst the various systems are presumably connected with the degree of adaptability of the shape and size of the host channel to that of the guest. The resultant polymers are usually highly crystalline and because of the geometrical constraints of the channel inclusion contain linear macromolecules with no branching. The polymer macroconformation (i.e., morphology) in an inclusion complex is determined by the geometry of the channels and so is different from that of the native polymer. This morphological difference influences the melting properties and can be observed in the low-angle X-ray diffraction patterns of the polymer. On removal of the host by dissolution in a suitable solvent, the polymer chains maintain their orientation and extended macroconformation but do not achieve ordered packing in the plane perpendicular to the chain axes.[3] Studies of the kinetics of reaction, the phenomenon of postirradiative polymerization, and the fact that the molecular weight of the product polymer is found to be directly proportional to the yield indicate that inclusion polymerization is a living polymerization,[4] that is, that termination and chain-transfer reactions are effectively suppressed. Wide-line ^1H NMR studies of the polymerization of acrylonitrile in urea indicate that the polymerization reaction is only initiated at temperatures at which the molecular motion of the included monomers becomes active.[5] The urea channels begin to be destroyed around the forming polymer, and the motion of the urea molecules is observed to be greater than before irradiation.

A combination of cross polarization, dipolar decoupling, and magic angle spinning (MAS) techniques[6] has enabled in favorable circumstances the acquisition of high-resolution NMR spectra from crystalline solids, allowing distinction of nuclei in different chemical environments in a molecule.[7] It has also made feasible the application to the solid state of many of the techniques and analyses for probing structural and dynamical properties of molecules that were developed in solution NMR spectroscopy.[8] Additionally, characteristics of the CP/MAS NMR experiment allow the exploration of features of the chemical systems only accessible in the solid state, where the rapid molecular tumbling, which is characteristic of most solution environments, is generally suppressed. The sensitivity of high-resolution solid-state NMR spectra to local structural effects and to any molecular dynamic process suggests that this technique could be of considerable value in studies of the constitutional and stereochemical specificity of inclusion polymerization, and the conformational and orientational properties, of the resultant polymers. Solid-state NMR could be used to study the inclusion compounds with the monomers, to observe intermediates in the polymerization proccess, to study the inclusion compounds with the resultant polymers, and to compare such polymers when separated from the host with the native polymers. Studies by both ^{13}C CP/MAS NMR[9,10] and ^2H NMR lineshape analysis[11] of the structure and the mobility of 1,4-*trans*-polybutadiene and 1,4-*trans*-polyisoprene included within perhydrotriphenylene have already demonstrated the differences between the included and extracted polymers.

A channel-type inclusion host with a somewhat flexible channel size is deoxycholic acid (DCA). It forms inclusion compounds of high thermal stability with a wide range of monomers. This leads to an observed ease of inclusion polymerization, under relatively nonstringent conditions and also to the stability of the inclusion compounds with the resultant polymers. Polymerization of dienes in DCA is constitutionally controlled, leading to 1,4 rather than 1,2 polymerization, and predominantly in the trans geometry. DCA occurs naturally as a single enantiomer, and polymerization of prochiral dienes yields optically active polymers. "Through-space" rather than "through-bond" chiral induction is implicated.[12] We present here some ^{13}C CP/MAS NMR studies on the well-known inclusion polymerization of 2,3-dimethylbutadiene in the inclusion complex with DCA.[13] The resultant poly(2,3-dimethylbutadiene) is highly crystalline with an almost

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exclusively 1,4-trans structure. Polymerization is achieved by irradiation at low temperatures and subsequent controlled postirradiative polymerization at a higher temperature. The nature of the resultant polymer has been probed from IR spectra, DTA and thermogravimetric analyses, viscosity measurements, solution ^{1}H NMR spectra, and X-ray diffraction studies.[13,14] Our results presented here suggest solid-state CP/MAS NMR spectroscopy to be a valuable addition to the techniques available to study the inclusion polymerization phenomenon.

Experimental Section

The compounds were handled on a dual vacuum/nitrogen line using standard Schlenk techniques.[15] Thermogravimetric analysis (TGA) measurements were performed on 10 mg of sample in a static air atmosphere with a Stanton Redcroft STA 785 simultaneous thermal analyzer.

Following the procedure of ref 13, 2,3-dimethyl-1,3-butadiene (Aldrich) was vacuum distilled to free it from the added inhibitor, hydroquinone. A total of 1.0 g of deoxycholic acid, 4 mL of methanol, and 0.4 mL of 2,3-dimethyl-1,3-butadiene were sealed in an ampule under vacuum. The ampule was placed in a water bath at 70 °C, producing a colorless solution. Recrystallization was induced by slow cooling to ambient temperature over 24 h and then to 0 °C for 5 h. The resultant crystals were very slim needles. Elemental analysis, performed by the analytical service of this laboratory (Found: C, 74.12%; H, 10.10%), is consistent with either $(DCA)_3$/DMB or $(DCA)_2$/DMB. TGA showed the characteristic weight loss, centered at 160 °C, which is indicative of the inclusion complex of DCA with DMB, and the actual weight loss in each case is consistent with the stoichiometry as close to 3:1 in the manner of ref 13. However, due to the features of the ^{13}C CP/MAS NMR spectrum to be described, it is suggested that the stoichiometry of the material is actually closer to $(DCA)_2$/DMB. Space-filling models show that a 2:1 complex is not an unreasonable proposition.

The $(DCA)_2$/DMB inclusion complex was sealed under vacuum in a 10-mm Pyrex ampule and was placed in a cold bath at −78 °C, a distance of 10 cm from a Gammabeam 150 ^{60}Co γ-ray source (the calculated dosage rate was 0.6 Mrad/h). Irradiation was maintained for 3 h. The sample was then warmed to 0 °C, at which temperature it was maintained for 24 h for the purposes of postirradiative polymerization. TGA confirmed the occurrence of the polymerization. The resultant polymer was freed from inclusion by dissolution of the DCA host lattice in boiling methanol.

All solid-state NMR spectra were recorded on a Bruker CXP200 pulse NMR spectrometer with an Oxford Instruments 4.7-T wide-bore (98-mm) superconducting solenoid magnet (200.13 MHz for ^{1}H NMR) and equipped with an Aspect 2000 data system. ^{13}C CP/MAS NMR spectra were recorded at 50.32 MHz using a multinuclear, proton-enhanced, double-bearing magic angle sample spinning probe (Bruker Z32-DR-MAS-7DB) and a high-power proton decoupler. A single contact spin-lock CP sequence[16] with alternate cycle spin temperature inversion and with flip-back of ^{1}H magnetization[17] and a proton radio-frequency (rf) field of 1.7 mT (ω_1 = 72 kHz), resulting in a 90° pulse length of 3.5 μs, was used. Temperature regulation, utilizing a Bruker B-VT1000 unit equipped with a copper–constantan thermocouple and digital reference, was of the bearing gas, and temperature measurement was of the bearing exhaust close to the sample. Temperature calibration below room temperature was achieved with the samarium ethanoate tetrahydrate Curie law chemical shift thermometer,[18] previously calibrated against the phase transition of D-camphor,[18] and above room temperature with the phase transitions of cobaltocenium hexafluorophosphate[19] and 1,4-diazabicyclo[2.2.2]octane.[18] The system was allowed to equilibrate at each new temperature for 1 h before spectral accumulation was commenced. The setting of the spinner angle was checked at each temperature using the ^{79}Br resonance of a small amount of KBr,[20] separated from the sample by a plastic disk. Approximately 350 mg of the compound was packed into a 7-mm zirconia rotor with a Kel-F top. ^{13}C CP/MAS NMR spectra were recorded in the temperature range from 219 to 336 K at typical MAS rates of ca. 3 kHz. Up to 2000 transients with a contact time of 1 ms (the optimum contact time for the DCA component) or 3 ms (the optimum contact time for the guest component) and a recycle delay of 3.5 s were acquired for each spectrum. In the case of the isolated polymer, 50 mg of polymer was dispersed amongst KBr packed into an Andrew-Beams type rotor of deuterated perspex (DPMMA) for use in a single bearing design of MAS NMR probe. Chemical shifts are reported on the δ scale with respect to δ(TMS) = 0 and were referenced to the secondary standard adamantane. In order to derive values of T_{CH} and $T_{1\rho}(^1H)$ from spectral intensities recorded at a range of contact times, the data were fitted to a simplified model of the cross-polarization dynamics[21]

$$I = K\{\exp[-t_{CP}/T_{1\rho}(^1H)] - \exp[-t_{CP}/T_{CH}]\}/[1 - T_{CH}/T_{1\rho}(^1H)]$$

where K is a constant. Dipolar dephasing experiments[22] (using delays of ca. 20–200 μs) were carried out using the pulse sequence of Alemany et al.[23] in which 180° pulses are simultaneously applied to the proton and observed spins halfway through the delay time in order to refocus the effects of chemical shifts and other static field inhomogeneities. For T_1 determinations using CP/MAS NMR, Harbison et al.'s[24] modification of Torchia's experiment[25] was used, for which $M_{net} = (M_1 - M_2) = 2M_{CP}\exp(-t/T_1)$.

Results

(a) Inclusion Compound $(DCA)_2$/DMB. The ^{13}C CP/MAS NMR spectrum of $(DCA)_2$/(DMB) (1) at 296 K is shown in Figure 1. The spectrum shows the excellent resolution typical of DCA inclusion compounds.[26] The resonance at 179.8 ppm can immediately be identified with the carboxyl carbon of the DCA. In addition, a closely-spaced pair of resonances at ca. 73 ppm typical of most DCA compounds is apparent, and the majority of the methine, methylene, and quaternary carbons of the DCA are clustered in the region of the spectrum from 22 to 50 ppm.[27] The methyl carbon resonances of the DCA and of the DMB are all in the region of the spectrum from 10 to 25 ppm. In addition, two resonances, one reasonably sharp ($\Delta\nu_{1/2}$ = 24 Hz) at 143.6 ppm and one somewhat broader ($\Delta\nu_{1/2}$ = 85 Hz) at 113.3 ppm, are observed and attributed to the unsaturated carbons of the DMB. Also, shown in Figure 2 is the spectrum after a delay for dipolar dephasing of 40 μs, in which only the resonances of the quaternary carbons and the carbons of the mobile methyl groups, in which the ^{13}C–^{1}H dipolar decoupling has been averaged, survive. From this spectrum we may assign C(13) and C(10), the two nonprotonated carbons of the DCA; C(13) resonates downfield of C(10).[28] In addition, the resonance at 143.6 ppm, which survives in the dipolar dephasing experiment, may be ascribed to the two nonprotonated alkene carbons of the DCA, C_q. Thus, the resonance at 113.3 ppm is that of the protonated alkene carbons, C_a.

The dipolar dephasing experiment shows six separate resonances that may be assigned to methyl carbons. Five are sharp ($\Delta\nu_{1/2}$ < 10 Hz), as expected for typical methyl groups. The resonance at 20.8 ppm is of lower intensity than the other resonances and is broader ($\Delta\nu_{1/2}$ = 15 Hz). The former five peaks show similar behavior in dipolar-dephased spectra; the resonance at 20.8 ppm is dephased considerably less than the others. This indicates a greater dynamic averaging of the ^{13}C–^{1}H dipolar coupling for the methyl groups represented by the latter resonance. The spin–lattice relaxation of the resonance at 20.8 ppm is not more rapid than for the other methyl resonances, in the manner that the dipolar dephasing is less rapid. The unique carbon resonance at 20.8 ppm is assigned to the methyl carbons of the DMB, which in addition to the simple "C_3" methyl group reorientation are evidently affected by a further molecular dynamical averaging

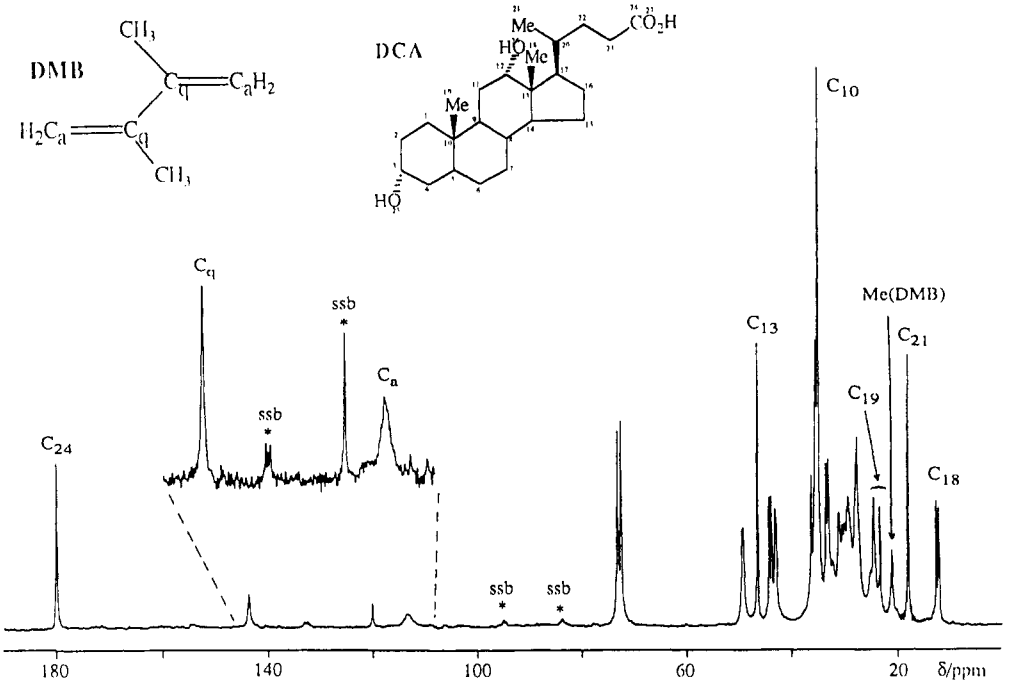

Figure 1. ^{13}C CP/MAS NMR spectrum of $(DCA)_2/DMB$ at 296 K with an expansion showing the spectral region containing the alkene carbon resonances of the DMB (*ssb indicates a spinning side-band peak).

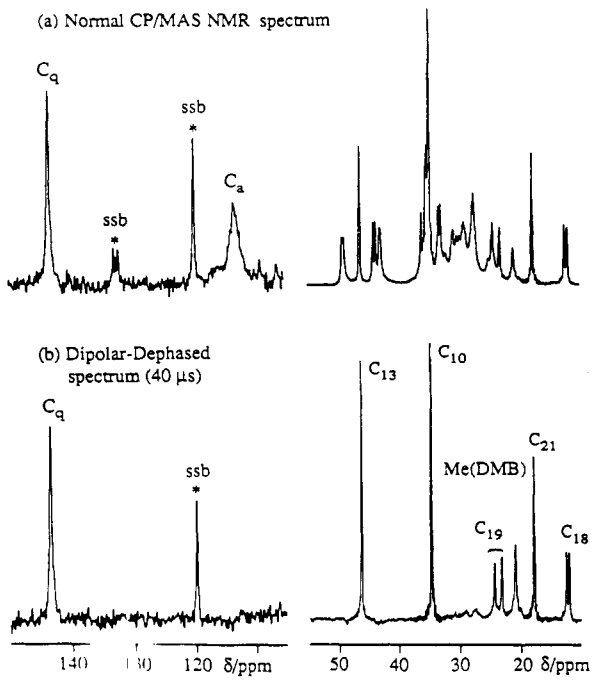

Figure 2. Comparison of (a) the normal ^{13}C CP/MAS NMR spectrum and (b) the dipolar-dephased spectrum with a dephasing delay of 40 μs for $(DCA)_2/DMB$ (*ssb indicates a spinning side-band peak).

process, which is occurring at a rate significantly slower than the Larmor frequency.

On comparison with assignments for the methyl carbons of the DCA from solution NMR studies, the resonance of doubled intensity at 17.8 ppm is assigned speculatively to C(21), the resonances at 24.2 and 23.05 ppm to C(19), and those at 12.5 and 12.0 ppm to C(18).[29] It is evident that the resonances of C(18) and C(19) are each of the form of a 1:1 doublet, though C(21), C(13), C(10), and C(24) are all singlet resonances. The positioning of the guest molecules of DMB in the DCA channels must create the presence of two inequivalent DCA molecules in the crystalline structure, which differ slightly from each other in the local environment proximate to C(19) and to a lesser extent C(18). This should be compared with the ^{13}C CP/MAS NMR spectrum for the inclusion complex $(DCA)_2$/ferrocene which shows a similar effect. For the latter the difference between inequivalent DCA molecules is sufficient to cause chemical shift differences for carbons of all the assigned resonances apart from C(13).[24] It would be impossible to obtain this 1:1 splitting of resonances for a complex of stoichiometry 3:1; hence, the suggestion that this material should be reformulated as $(DCA)_2/DMB$.

Selected regions of the ^{13}C CP/MAS NMR spectra for 1 at temperatures between 219 and 336 K are shown in Figure 3. The spectrum for the DCA component of the compounds changes only slightly with temperature. Some subtle changes are noticeable in the resonance profile of the methine/methylene/quaternary carbon region, perhaps indicative of some small temperature-induced changes in chemical shifts. At temperatures below ambient the splitting between the two resonances of the 1:1 doublet of C(19) decreases and the splitting for the similar doublet of C(18) increases, such that the splittings in the two cases become more similar. At temperatures above ambient the doublet splitting for C(19) increases and that for C(18) becomes extremely small, such that the splittings in the two cases become more disparate. Since the difference in local environments of the two distinct DCA molecules in the structure of 1 is most likely due to the presence of the guest molecules, this implies small, but clearly significant, temperature-dependent changes in the position of the guest DMB molecules relative to the DCA host lattice. The differences in local environment between the two DCA molecules in the structure are evidently larger for C(19) methyl groups at higher temperatures and for C(18) groups at lower temperatures.

The resonances of the DMB carbons change in a somewhat more dramatic manner. The line width of the methyl carbon resonance changes with temperature. At 219 K this resonance is as narrow as the resonances of the methyl carbons of the DCA ($\Delta\nu_{1/2}$ = 10 Hz), at 258 K it is significantly broader ($\Delta\nu_{1/2}$ = 14 Hz), and at 296 and 336 K it is very slightly broader still ($\Delta\nu_{1/2}$ = 15 Hz). The resonance for the nonprotonated alkene carbon, C_q, is as broad at 219 K as at room temperature ($\Delta\nu_{1/2}$ = 24 Hz),

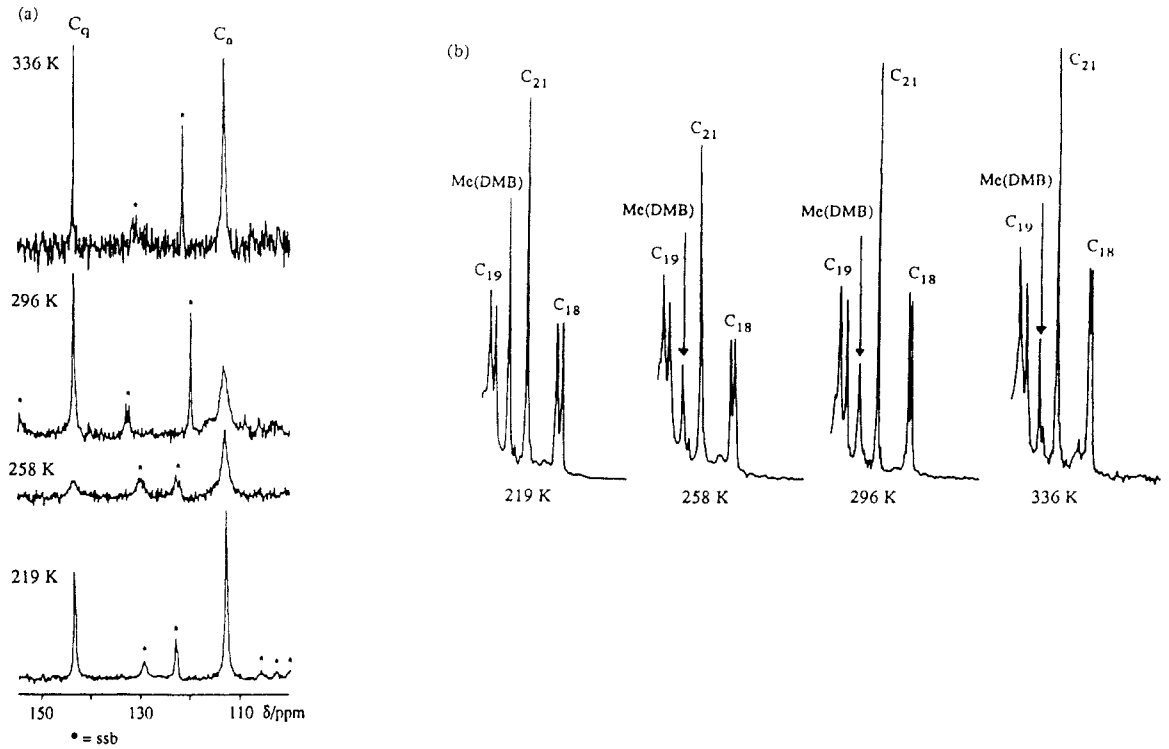

Figure 3. ^{13}C CP/MAS NMR spectra for $(DCA)_2$/DMB at temperatures from 219 to 336 K, showing (a) the alkene region of the spectrum and (b) the methyl region of the spectrum.

but at 258 K it is extremely broad ($\Delta\nu_{1/2} > 100$ Hz). It sharpens again with an increase in temperature and by 336 K is sharp ($\Delta\nu_{1/2} = 10$ Hz). The other alkene carbon resonance, C_a, is relatively narrow at 219 K ($\Delta\nu_{1/2} = 25$ Hz), and so all three carbon resonances of the DMB molecule are relatively sharp at this temperature. At 258 K the C_a resonance is broader ($\Delta\nu_{1/2} = 80$ Hz), but considerably narrower than the C_q resonance at the same temperature. By 296 K the C_a resonance is still very broad ($\Delta\nu_{1/2} = 85$ Hz), at which temperature the C_q resonance is considerably sharper. Eventually at 336 K the C_a resonance has become sharper ($\Delta\nu_{1/2} = 30$ Hz). The broadening effects at any given temperature change with different ^1H-decoupling fields, and we thus explain them as being a consequence of molecular dynamics, which when of equivalent rate to the proton-decoupling rf field frequency ($\Delta\omega \approx 40$–70 kHz) prevent the effective dipolar decoupling of carbon-13 from proton spins.[30,31] This may arise either by motion involving the carbon spin itself or by relative motion of the protons to which it is coupled.

If a single dynamic process were the cause of the broadening of all of the DMB ^{13}C NMR resonances, we would expect the maximum extent of broadening to occur at the same temperature for each resonance; the extent of that broadening would depend upon the strength of the dipolar coupling of the carbon to protons in each case. Thus, although all three resonances are close to their maximum extent of broadening[33] at 258 K, the rates of change of the line widths of the different resonances with rise and fall in temperature from 258 K are somewhat disparate. All three resonances become relatively sharp by 219 K. The C_q resonance also sharpens rapidly with an increase in temperature, the C_a resonance sharpens somewhat less rapidly, only becoming appreciably narrowed at 336 K, and the methyl carbon resonance shows no sharpening at all to temperatures of 336 K. We can explain this observation in a qualitative manner if we assume that the behavior at temperatures below about 258 K reflects in the major part a single dynamic process which affects all the carbon resonances and which gradually increases in rate with increasing temperature, matching the frequency of the dipolar decoupling rf field ($\omega_1 \approx 72$ kHz) to yield maximum dipolar broadening at about 258 K. Above this temperature the effects of a second dynamic process of somewhat lower rate than the first become apparent. This process affects only C_a and the methyl carbons, and of the two apparently affects the methyl carbons most. The broadening in the dipolar decoupling regime due to this second dynamic process starts to become significant on the dipolar decoupling time scale at ca. 258 K and apparently matches the frequency of the dipolar decoupling rf field in the region of ambient temperature. This explains the narrowing of the C_q resonance with increasing temperature above 258 K, while those of C_a and the methyl carbons remain broad. Even this model is simplified and does not explain all the details of the changes in line width of the carbon resonances of the DMB. For example, the observation that at 258 K the resonance of C_q is actually broader than that of C_a cannot be easily explained, since the quaternary carbon, C_q, would be expected to be considerably less strongly dipolar coupled to protons than C_a, which has directly-bonded hydrogens. The supposition that two or more dynamic processes affect the spectra does also help rationalize the complex nature of the differences between spectra recorded at the same temperature, but with different values of the proton decoupling rf field.

For the C_q and C_a resonances the chemical shift anisotropy (CSA) was also monitored from the MAS sideband profile. Throughout the temperature range studied there is no detectable change in CSA for either resonance. We thus assume that above 219 K any averaging of the CSA of these carbon resonances by the invoked dynamic processes is at rates in the fast limit on the CSA time scale ($> \approx 10^4$ Hz). The anisotropy of the C_a resonance is clearly less than that of the C_q resonance; this is consistent with further averaging of the CSA of the C_a resonance by the second dynamic process in which the C_q carbons are assumed not to participate. The nature of the dipolar dephasing and spin–lattice relaxation behavior of the

methyl carbon resonance of DMB, as referred to earlier, is also well explained on this basis. At 296 K the rates of the invoked molecular dynamic processes are greater than ca. 70 kHz and the $^{13}C-^{1}H$ dipolar coupling is being extensively averaged by these molecular dynamic processes as well as by the rapid methyl "C_3" reorientation, hence, the high degree of suppression of dipolar dephasing observed for this resonance. However, the rates of these processes, unlike the rate of methyl reorientation, are too low ($\ll$50 MHz) to cause efficient spin–lattice relaxation.

With regard to the possible nature of these dynamic processes we must consider both "internal" molecular dynamic processes and the overall molecular reorientation of the DMB molecules within the host lattice. As has been shown by ^{2}H NMR for several molecular species included in DCA,[26,34] there is, at the very least, some scope for restricted reorientation of the guest molecules relative to the host lattice. That reorientation of the DMB molecules in 1 might occur is supported by our interpretation of the changes in the splittings of the 1:1 doublets in the resonances of C(19) and C(18) methyl carbons of the DCA on change in temperature as indicating positional changes of the DMB molecules in the lattice. Such a molecular reorientation could correspond to the lower energy dynamic process discussed above, because it clearly involves spatial movement of all the carbon atoms in a DMB molecule.[35] The most facile internal reorientational flexibility of the molecule, apart from the methyl group "C_3" reorientations, is expected to be about the central C_q-C_q single bond. The stereoregularity of the inclusion polymerization of such butadiene-type monomers is attributed to hindrance of rotation about the C_q-C_q bond, due to the steric confinement, caused by the close proximity of the channel walls of the host structure, restricting the diene to an anti conformation about this bond. Torsional oscillation about this bond might occur, though certainly not so spatially-extended as to effect anti $\leftrightarrow$ syn conformational interchange. This motion could identify with the second dynamic process implicated by the CP/MAS NMR spectra discussed above, because only the C_a and methyl carbons are spatially averaged by such a process.

It has been suggested previously, first, that the stereoregularity of inclusion polymerization requires an ordered monomer arrangement within the channels, second, that the restriction of conformational freedom of the monomer by the proximity of the channel walls causes it to adopt an anti conformation about the central single bond, which ensures a 1,4-trans monomer unit in the polymer, and, third, that polymerization is only initiated at temperatures at which molecular motion of the monomers becomes active. All three factors may be rationalized by the features we observe in the ^{13}C CP/MAS NMR spectrum of 1:

(i) The ordering of the DMB monomers in the DCA channels is indicated by the splitting of the C(19) and C(18) methyl carbon resonances of the DCA into 1:1 doublets, which is assumed to be due to two types of DCA molecules in the asymmetric unit of the crystal structure, made inequivalent by local environment effects from the positioning of the DMB molecules. The splittings of the doublets change with temperature, indicating a change in positioning or the onset of dynamics of the DMB molecules with respect to the host lattice at different temperatures. Random positioning of the DMB molecules within the host lattice would lead to a range of environments and correspondingly no splitting but generally broad NMR resonances for the DCA carbons affected.

(ii) A dynamic process which affects only the C_a and methyl carbon resonances of the DMB is implicated by the variable-temperature ^{13}C CP/MAS NMR spectra. This could correspond to restricted motion about the central C_q-C_q single bond. However, the nature of the averaged CSA for C_a suggests that it does not involve oscillations of sufficient amplitude to transfer DMB molecules from the anti to the syn conformer.

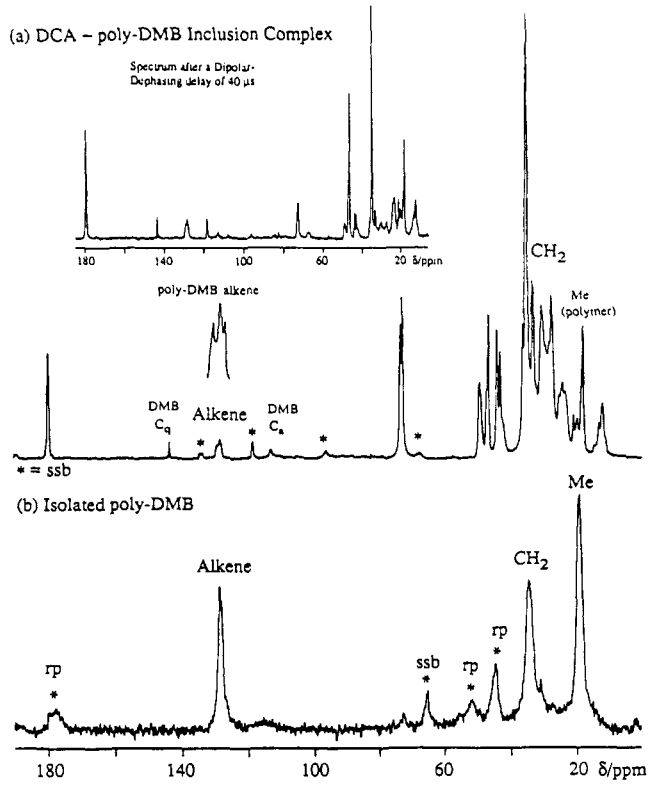

Figure 4. Comparison of the ^{13}C CP/MAS NMR spectrum for (a) postirradiatively polymerized $(DCA)_2$/DMB, and an inset of the same spectrum after a delay for dipolar dephasing of 40 μs, (b) DMB polymer isolated from the inclusion complex by washing with boiling methanol. The figures show assignments for the resonances of the carbon functionalities of the polymer. (*ssb indicates a spinning side-band peak; *rp indicates residual peaks from the rotor material, DPMMA).

(iii) A dynamic process, which affects the resonances of all the carbons of the DMB, is also implicated by the NMR data. Such a motion is most likely to be an overall molecular reorientation of the DMB guest molecules in the host lattice. There is precedent for such motion of simple organic molecules included in DCA.[34] The increase in rate of both dynamic processes and the change in positional ordering of the DMB monomer with respect to the host lattice with an increase in temperature may be seen to be reflected in the increase in rate of postirradiative polymerization observed for increases in temperature.

(b) NMR of the Inclusion Polymer and the Free Polymer. A ^{13}C CP/MAS NMR spectrum of the postirradiatively polymerized material is shown in Figure 4. Comparison of the spectrum of the irradiated material with the spectrum of the simple inclusion compound of the DMB monomer shows many differences. First, the intensities of the resonances of the DMB monomer are dramatically reduced. The remaining intensity of these monomer resonances does show that the relative line widths of the C_a, C_q, and methyl resonances are preserved for the residual monomer molecules in the material, although the C_q alkene resonance is even sharper ($\Delta\nu_{1/2}$ = 10 Hz) than is the case in the spectrum of 1. The resonances of the DMB monomer have been largely superseded by new resonances which may be assigned to poly(2,3-dimethylbutadiene). An intense resonance at 18.8

ppm, which survives in the dipolar-dephased spectrum at 40 μs, is assigned to the polymer methyl carbons. It is broad by comparison to the other methyl carbon resonances ($\Delta\nu_{1/2} \approx 35$ Hz). The methylenic carbons of the polymer would be expected to resonate within the major region of intensity from the DCA carbons. On comparison with the spectrum of 1 the most striking new feature in the form of this region of the spectrum is the appearance of a resonance at 35.5 ppm. Given that the conformational structure of the DCA molecules is not expected to undergo large changes on the change of the guest molecule in the inclusion,[36] we assign this new resonance to the methylenic carbons of the included polymer. Finally a multiplet centered at approximately 128.5 ppm, which is only slowly dipolar dephased, is assigned to the alkene carbons of the polymer. This resonance is composed of at least three closely spaced resonances; at 127.7, 128.3, and 129.2 ppm. Comparison of the intensity of the alkene resonance of the polymer with the combined intensities of the alkene resonances of the DMB monomer allows estimation of the conversion of the DMB monomer into polymer as ca. 66%, in good accord with measurements from TGA.[13,14]

The resonances of the DCA component also show a change relative to the spectrum of 1. The most noticeable feature is that the main methylene/methine/quaternary carbon region of the spectrum due to the DCA is relatively less well resolved. This may arise simply as a consequence of the presence of two types of included guest molecules, namely, DMB and polyDMB. As before, the quaternary and methyl carbon resonances of the DCA may be identified from the dipolar-dephased spectrum at 40 μs. Of these, the quaternary C(13) carbon shows a shoulder to low field, where previously in 1 it had been a single resonance. C(10) is still ostensibly a single peak, but the methyl carbon resonances C(19), C(21), and C(18) are highly complex. Major changes in the hydrogen-bonded "double sheets" of DCA that make up the host lattice are not expected on introduction of a new included guest molecule, but the change of the guest molecule will cause a change in the local environment of the DCA molecules. Such local structure effects are well-known to be detected with extreme sensitivity in the methyl carbon ^{13}C CP/MAS NMR chemical shifts.[37]

The ^{13}C CP/MAS NMR spectrum of the DMB polymer isolated from the DCA by washing with methanol is also shown in Figure 4. There are three regions of intensity in the spectrum, a resonance at 19.0 ppm, which may be attributed to the methyl carbons, a resonance at 34.2 ppm, which confirms the assignment of the methylene carbons in the spectrum of the polymer inclusion (both of these resonances are at essentially the same chemical shift as the corresponding resonances in the inclusion complex of the polymer with DCA), and a resonance at 128.2 ppm, which may be attributed to the alkene carbons. All the resonances are relatively broad ($\Delta\omega_{1/2} \approx 70$ Hz) but are narrow enough to indicate that the polymer is relatively crystalline. Additionally, each resonance has a small shoulder to high field, accounting for about 10% of the spectral intensity. By analogy with the results of ^{13}C CP/MAS NMR studies of 1,4-*trans*-polybutadiene isolated after formation by inclusion polymerization in perhydrotriphenylene,[9] these may be assigned to an amorphous region of the polymer. The most obvious difference between the spectra for the polymer when included in DCA and when isolated by dissolution of the DCA is the appearance of the alkene region of the spectrum. The alkene resonance for the included polymer apparently consists of at least three separate resonances, whereas for the free polymer there is just a single resonance. As previous work shows that the polymer should remain in the original extended macroconformation forced by the included environment,[13,14] this suggests that the origin of the multiple alkene resonance in the former case is not due to macroconformational effects but is more likely a reflection of different local environments due to different relative positions of the molecules of the DCA host for individual units of the polymer, as is also reflected in the complex nature of the methyl carbon resonances for the DCA molecules. This strongly suggests that the DMB polymer chains are not free to diffuse about the chain axis, as polybutadiene chains included in perhydrotriphenylene may.[9] This is presumably as a result of steric factors involving the substituent methyl groups in a similar manner to that proposed for polyisoprene in trihydrophenylene.[10,38]

Conclusion

The results of this study of the inclusion polymerization of 2,3-dimethylbutadiene in deoxycholic acid show that NMR can provide structural information in terms of local environmental and dynamical features for the monomer inclusion complex, for the polymer inclusion complex, and for the isolated polymer. Clearly solid-state NMR spectroscopy will play a major role in the further clarification of the modus operandi of these fascinating, highly specific solid-state reactions.

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References and Notes

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