Spectral Editing in Solid-State ^{13}C MAS NMR of Elastomers

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ABSTRACT: Spectral editing techniques combined with magic-angle spinning (MAS) are introduced for assigment of the individual resonances in solid-state ^{13}C NMR spectra for the amorphous (mobile) phases of elastomers. The proposed MAS SEMUT and MAS ESCORT pulse techniques allow unambiquous classification of the ^{13}C resonances according to the number of protons attached to the contiguous carbon. The methods are demonstrated experimentally for samples of natural rubber (*cis*-1,4-polyisoprene), polychloroprene (neoprene) rubber, ethylene-propylene rubber, styrene–butadiene rubber, tire rubber, and kariten (mainly *trans*-1,4-polyisoprene).

Introduction

During the past years pulse techniques for spectral editing,[1-8] i.e., separation of ^{13}C resonances according to the number of attached protons (multiplicity determination), have gained considerable popularity as a tool for assignment of liquid-state ^{13}C NMR spectra. This includes, for example, spectral editing of ^{13}C NMR spectra for elastomers in solution.[9-12] Spectral editing or multiplicity determination using the DEPT pulse sequence[3,4] has also been performed using static[12,13] and magic-angle spinning (MAS)[14] NMR for solid elastomers heated to about 60 °C in order to increase the chain mobility and thereby their isotropic ("liquidlike") behavior. Recently, the techniques have been extended to include solid-state cross-polarization (CP) MAS NMR experiments[15] for spectral editing of solids with relatively high intrinsic molecular mobility. For solid samples labeling of the $^{13}CH_n$ (n = 0, 1, 2, and 3) multiplets during a conventional spin-echo editing sequence requires averaging of interactions from dipolar coupling and ^{13}C chemical shielding anisotropy. This can be accomplished using a combination of MAS, rotor synchronization, homonuclear multipulse decoupling, and high-power ^1H decoupling (HPD).[16,17] For rigid solids, however, the experimental requirements for sufficient averaging to resolve the J multiplets may represent a difficult task.[18] For such samples some degree of spectral editing may be achieved using techniques exploiting heteronuclear dipolar interactions for multiplet labeling such as the recently introduced cross-polarization/depolarization (CP/CPD)[19,20] and asynchronous MASSLF[21] pulse sequences.

It is well-established that for the amorphous phase of bulk elastomeric compounds the dipolar interactions are substantially averaged by rapid reorientation of the molecular chain segments.[22-24] In fact, near isotropic conditions can often be obtained using MAS alone,[24] thereby rendering elastomers well-suited for a variety of liquid-state type NMR experiments such as spectral editing techniques. In this paper we present what to the best of our knowledge is the first MAS ^{13}C spectral editing experiments applied to elastomers in the solid state. Edited spectra, obtained using the SEMUT[5,6] and ESCORT[7] pulse techniques combined with MAS and HPD, are reported for various industrially important elastomers at ambient temperature.

Experimental Section

A. Samples. Six elastomers of commercial origin have been examined in this work. The samples are natural rubber (NR, *cis*-1,4-polyisoprene), polychloroprene (neoprene) rubber (CR), ethylene–propylene rubber (EPR), styrene–butadiene rubber (SBR), tire rubber, and kariten. Kariten is a crude mixture of *cis*- and *trans*-1,4-polyisoprene (in a ratio of approximately 1:7) obtained in large quantities as a distillation residue in production of vegetable oil. The solid elastomers were used without further purification and were cut into small pieces before packing into the MAS rotor. A dissolved sample of kariten, approximately 3% w/w in $CDCl_3$, was also examined.

B. Instrumentation. High-resolution ^{13}C NMR experiments were performed using a Varian XL-300 (7.05-T) spectrometer operating at 75.43 MHz for ^{13}C. The solid-state NMR experiments were carried out at ambient probe temperature (ca. 25 °C) using a home-built high-speed spinning CP/MAS probe[25] with 7-mm-o.d. Si_3N_4 rotors (220-μL sample volume) capable of handling imbalance from imperfect packing of the rubber pieces. Spinning speeds (ν_r) in the range of 3.5–4.5 kHz were employed. The ^{13}C channel radio-frequency field strength was typically 42 kHz, corresponding to a 90° pulse width $t_{90}(^{13}C)$ = 6.0 μs, and the ^1H radio-frequency field strength used for editing pulses and HPD was 33 kHz, corresponding to $t_{90}(^1H)$ = 7.6 μs. ^{13}C chemical shifts are in ppm relative to an external sample of tetramethylsilane (TMS).

C. Experimental Techniques. The two spectral editing techniques employed in this work have been analyzed in detail in separate papers, where rigid solid[15] and liquid[5-7] versions of the experiments are considered. In this section we briefly review some of the main features of the techniques applicable to the amorphous/mobile phases of elastomers.

Pulse schemes for the MAS SEMUT and MAS ESCORT experiments are shown in parts a and b of Figure 1, respectively. The sequences are identical to their liquid-state analogues apart from (i) MAS is applied to average dipolar interactions and chemical shielding anisotropy, (ii) detection is performed under HPD, and (iii) the ^1H decoupler is turned off during the relaxation delay to protect the radio-frequency circuitry. In both experiments transverse ^{13}C magnetization, created by an initial 90° (^{13}C) pulse, evolves under the influence of heteronuclear scalar J couplings during a spin-echo editing fragment. The efficiency of this evolution can be controlled by varying the length of the θ-editing pulse in MAS SEMUT (Figure 1a) or the length of the decoupler-off period τ in MAS ESCORT (Figure 1b), while maintaining a constant length of the overall spin-echo periods. Discrimination of ^{13}C signals from the various one-bond coupled CH_n (n = 0, 1, 2, and 3) spin systems is achieved by appropriate linear combinations of MAS SEMUT experiments recorded using flip angles of θ = 0°, 60°, 120°, and 180° with relative number of scans 1:2:2:1[5] or MAS ESCORT experiments recorded using θ = 0°, 60°, 120°, 180°, 240°, and 300° (θ = 180°$J\tau$) with relative number of scans 1:10:4:1:2:2.[7] Under ideal conditions complete editing into subspectra, containing only one multiplicity, requires a combination of spectra from these subexperiments using the coefficients listed in Table I.[5,7] In practice the coefficients may differ somewhat from the ideal values, and in this study we employed a least-squares procedure for an optimum linear combination of the subexperiments.

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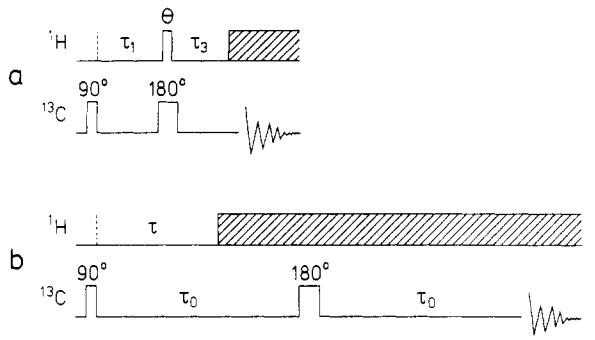

Figure 1. Pulse sequences (a) MAS SEMUT and (b) MAS ESCORT employed for subspectral editing of ^{13}C NMR spectra for elastomers. The τ delays in MAS SEMUT should be chosen as $\tau_1 = \{2[J_{min} + 0.146(J_{max} - J_{min})]\}^{-1}$ and $\tau_3 = \{2[J_{max} - 0.146(J_{max} - J_{min})]\}^{-1}$ to reduce J cross-talk.[5,6] The actual range for the heteronuclear (^{13}C–^{1}H) J coupling constants is given by $J_{min} < J < J_{max}$. The fixed delay τ_0 in MAS ESCORT should be adjusted to $\tau_0 = 5(3J)^{-1}$ for complete editing into individual CH_n (n = 0, 1, 2, and 3) subspectra, whereas $\tau_0 = (J)^{-1}$ should be used for editing into n even (C, CH_2) and n odd (CH, CH_3) subspectra ($J = (J_{min} + J_{max})/2$). For MAS ESCORT the "editing angle" is defined as $\theta = 180°J\tau$.

Table I
Ideal Coefficients for a Linear Combination of MAS SEMUT and MAS ESCORT Subexperiments Leading to Complete Spectral Editing[5,7]

	θ^b			
multiplicity[a]	{0°}	{180°}	{60°},{300°}	{120°},{240°}
3/5 C	−1/10	−1/10	2/5	2/5
1/3 CH	−1/18	1/18	4/9	−4/9
3/8 CH_2	1/4	1/4	−1/4	−1/4
1/4 CH_3	1/6	−1/6	−1/3	1/3

[a] The factors reflect ideal signal intensities observed in the completely edited subspectra.[5,7] [b] The θ = 300° and θ = 240° subexperiments, which apply only for MAS ESCORT, use the same coefficients as the θ = 60° and θ = 120° subexperiments, respectively.

An intrinsic feature of the Figure 1 spectral editing sequences is that the highly mobile carbons associated with the amorphous phase of the elastomers are selectively probed. Signals from rigid bound protonated carbons undergo efficient dipolar dephasing throughout the long periods without HPD of the spin-echo editing fragments.[26] In contrast, less mobile (e.g., crystalline) phases may be observed selectively using excitation via CP,[27] and possibly the CH_n multiplicities may be labeled using MAS SEMUT with homonuclear multipulse decoupling and rotor synchronization of the spin-echo periods.[15] For the simple MAS SEMUT sequence all subexperiments contain a decoupler-off period of 6.5–8.5 ms, which usually leads to efficient dephasing for less mobile parts of the sample. For MAS ESCORT the spin-echo period is usually on the order of $2\tau_0 \approx$ 22–28 ms with a variable decoupler-off period (τ) leading to efficient dipolar dephasing (rigid parts) for all subexperiments except for the τ = 0 (θ = 0°) experiment. Anyway, the very long spin-echo period for this experiment usually causes suppression of "rigid" carbons due to rapid transverse T_2 relaxation.

One point of concern when applying ^{13}C spectral editing techniques to solid elastomers is their performance for carbons with short transverse relaxation times (T_2). Another point is the influence of radio-frequency field inhomogeneity. In cases of short T_2's, the MAS SEMUT sequence with a total length (ideally) of $1/J$ is preferred over the alternative DEPT[3,4] (length $3/(2J)$) and MAS ESCORT (length $10/(3J)$) techniques. MAS ESCORT is the technique of choice in the case of longer T_2's because the editing fragment of this sequence is not influenced by radio-frequency inhomogeneity.

Results and Discussion

The MAS SEMUT and MAS ESCORT editing techniques are demonstrated experimentally for NR, CR, EPR, SBR, tire rubber, and kariten in Figures 2–9. In addition, for most of the samples a standard HPD ^{13}C MAS spectrum was recorded to evaluate influences from relaxation and dipolar dephasing throughout the editing sequences. ^{13}C chemical shifts and assignments obtained from the spectra are summarized in Table II.

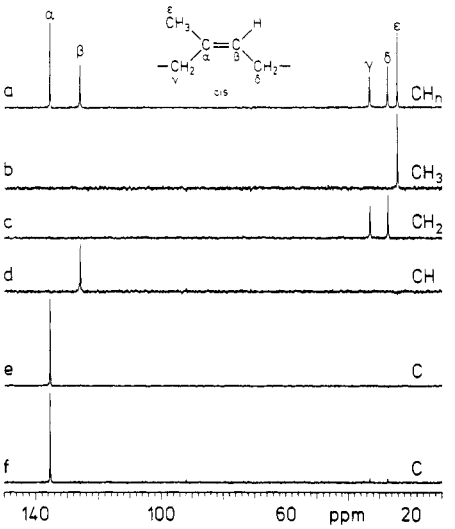

Figure 2. ^{13}C MAS ESCORT edited spectra of NR (J = 135 Hz, τ_0 = 15 ms, ν_r = 3485 Hz, and 4-s relaxation delay). (a) The θ = 0° (τ = 0) subexperiment (32 scans) with "unity" intensity for all carbons. (b–e) Complete edited subspectra obtained from a linear combination of $\theta = 180°J\tau = n60°$ (n = 1, ..., 5) subexperiments (see text). (f) Quaternary carbon spectrum resulting from the special quaternary-only version[7] of the MAS ESCORT experiment.

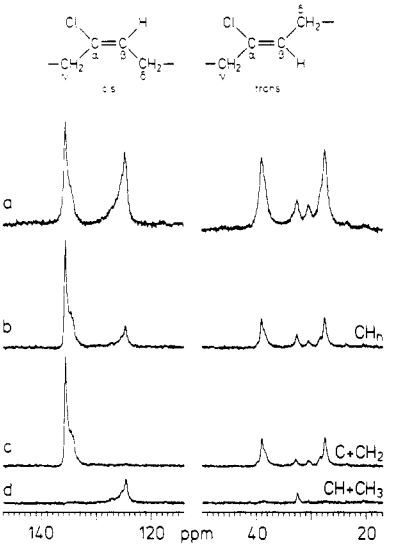

Figure 3. ^{13}C MAS NMR spectra of CR. (a) Standard ^{13}C MAS spectrum (ν_r = 4150 Hz, 896 scans, 4-s relaxation delay). (b–d) MAS SEMUT spectra showing (b) all CH_n resonances and (c and d) partially edited spectra containing CH_n resonances with (c) even and (d) odd parity of n. The c and d spectra were obtained as the sum and the difference, respectively, of θ = 0° and θ = 180° experiments (ν_r = 4150 Hz, τ_1 = 4.02 ms, τ_3 = 3.43 ms, 2400 scans, 6-s relaxation delay).

A. Natural Rubber (NR; *cis*-1,4-Polyisoprene). Figure 2 shows the edited MAS ESCORT ^{13}C spectra for NR obtained using the Figure 1b pulse sequence and ν_r = 3485 Hz. The "standard" CH_n spectrum in Figure 2a is that of the θ = 0° (τ = 0) MAS ESCORT experiment, while the fully edited CH_3, CH_2, CH, and C subspectra are shown in Figure 2b–e. As an alternative quaternary carbon (C) spectrum, the spectrum in Figure 2f was obtained using a special quaternary-only version[7] of the MAS ESCORT

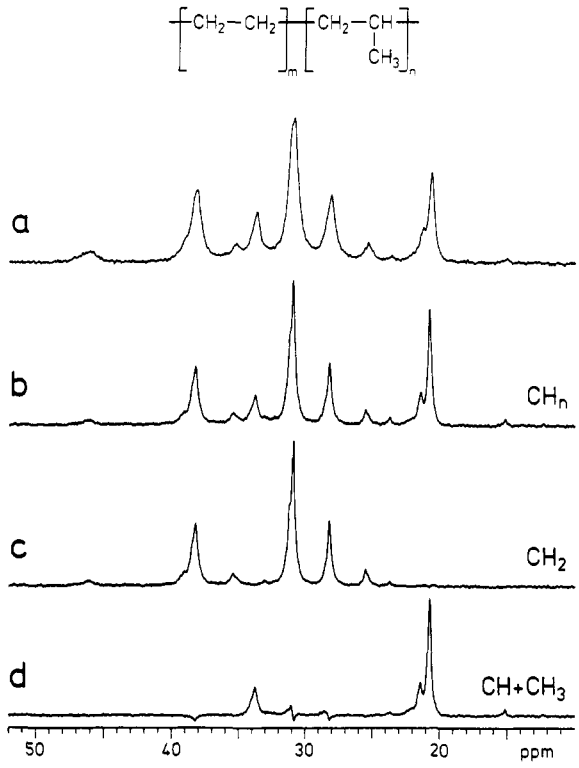

Figure 4. ^{13}C MAS NMR spectra of EPR. (a) Standard ^{13}C MAS spectrum (ν_r = 3510 Hz, 512 scans, 4-s relaxation delay) (b) θ = 0° MAS SEMUT spectrum (ν_r = 3510 Hz, τ_1 = 4.09 ms, τ_3 = 3.76 ms, 4096 scans, 4-s relaxation delay). (c and d) Partially edited CH_2 (c) and CH + CH_3 (d) MAS SEMUT subspectra. The minor negative or dispersive signals in d are ascribed to J cross-talk.[5]

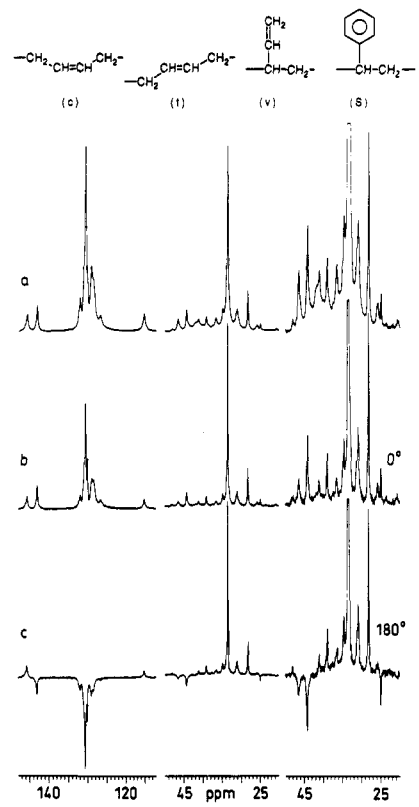

Figure 5. ^{13}C MAS NMR spectra of SBR. (a) Standard ^{13}C MAS spectrum (ν_r = 4340 Hz, 4096 scans, 4-s relaxation delay). (b and c) ^{13}C MAS SEMUT spectra using (b) θ = 0° and (c) θ = 180° (same parameters as in a). The spectra in the right column are identical to those in the center column but with a vertical scale expansion by a factor of 5.

experiment. The spectra demonstrate that spectral editing provides unambiguous assignment of the C, CH, and CH_3 resonances to C_α, C_β, and C_ϵ, respectively, for NR (stuctural formula is indicated in Figure 2). The C_γ and C_δ resonances in the CH_2 subspectrum may be distinguished according to standard additivity rules.[28] The result of the spectral editing is consistent with the assignment reported for bulk polyisoprenes in an early study by Duch and Grant.[23] When combined with MAS, rapid reorientation of the chain segments makes spectral editing based on heteronuclear J modulation during the τ period of the MAS ESCORT experiment a simple task as demonstrated here for NR at room temperature.

B. Polychloroprene (Neoprene) Rubber (CR). Proton-decoupled ^{13}C MAS NMR spectra of CR are illustrated in Figure 3. The $^{13}CH_n$ (all-carbon) spectra in parts a and b of Figure 3 are those of a standard ^{13}C MAS experiment and the corresponding θ = 0° MAS SEMUT experiment, respectively. The partially edited ^{13}C MAS SEMUT spectra shown in parts c and d of Figure 3 were edited according to CH_n fragments with n even (C and CH_2) and n odd (CH and CH_3), respectively, using the θ = 0° and θ = 180° subexperiments. Inspection of these subspectra along with standard additivity rules[28] enables assignment of the four major resonances to the C_α (135.6 ppm), C_β (124.7 ppm), C_γ (39.0 ppm), and C_δ (27.5 ppm) carbons of "pure" *trans*-1,4-CR in accordance with the assignments given by Coleman et al.[29] (the Greek letters refer to the structural formula). Here the term pure means that the *trans*-1,4-CR monomeric units are linked exclusively in a head-to-tail fashion. The spectrum also displays a number of weaker, more or less resolved signals and shoulders which indicate structural irregularities throughout the sample. These resonances most likely result from head-to-head and tail-to-tail linkages of *trans*-1,4-CR or from polymerization with *cis*-1,4-, 1,2-, or 3,4-CR units. For simplicity, we denote the tail–head configuration, $-CH_2C^tCl{=}C^h-$

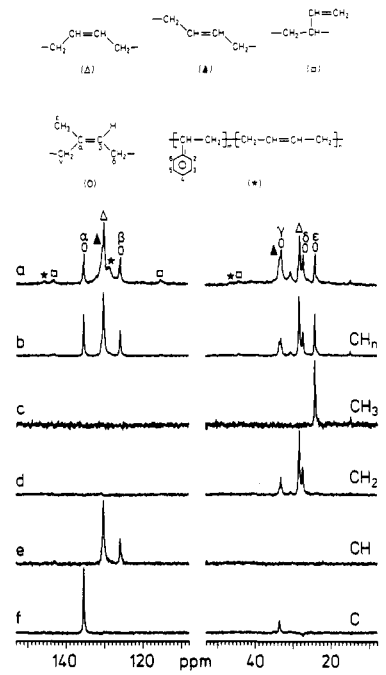

Figure 6. ^{13}C MAS NMR spectra of a tire rubber. (a) Standard ^{13}C MAS spectrum (ν_r = 3500 Hz, 524 scans, 4-s relaxation delay), (b) θ = 0° (τ = 0) MAS ESCORT spectrum. (c–f) Complete $^{13}CH_n$ (n = 3, 2, 1, and 0) edited MAS ESCORT subspectra. The MAS ESCORT experiments employed ν_r = 3510 Hz, τ_0 = 15 ms, 2-s relaxation delay, and 6720 scans distributed between θ = n60° (n = 0, ..., 5) subexperiments in a ratio of 1:10:2:1:2:2. The symbols △, ▲, and □ refer to *cis*-1,4, *trans*-1,4, and 1,2 units of polybutadiene, whereas ★ refers to styrene units in SBR.

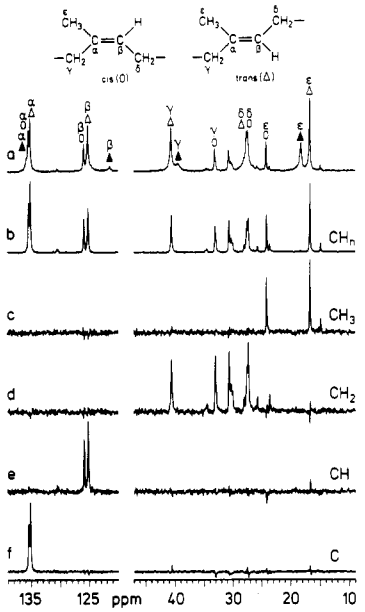

Figure 7. ^{13}C MAS NMR spectra of kariten. (a) Standard ^{13}C MAS spectrum (ν_r = 4190 Hz, 9600 scans, 6-s relaxation delay). (b) MAS SEMUT spectrum for the $\theta = 0°$ subexperiment and (c–f) completely edited CH_3, CH_2, CH, and C MAS SEMUT subspectra (ν_r = 4400 Hz, τ_1 = 3.54 ms, τ_3 = 3.98 ms, 9200 scans distributed between $\theta = 0°$, 60°, 120°, and 180° subexperiments in a ratio of 1:2:2:1). The O, Δ, and ▲ symbols denote amorphous *cis*-1,4-polyisoprene, amorphous *trans*-1,4-polyisoprene, and crystalline α-*trans*-1,4-polyisoprene, respectively. Greek letters refer to the structural formulas shown above the spectra. Minor signals from CH_m groups in the CH_n ($m < n$) subspectra result from J cross-talk.[5]

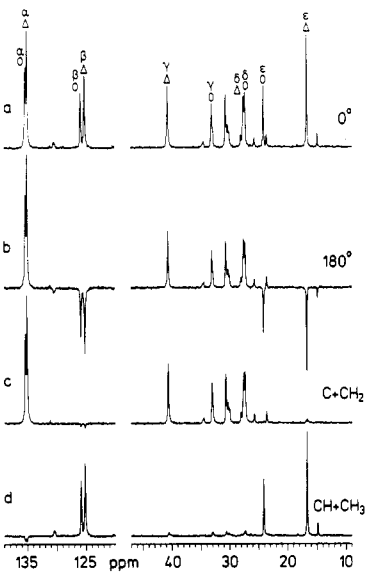

Figure 8. ^{13}C MAS SEMUT spectra of kariten. (a) $\theta = 0°$ spectrum showing all $^{13}CH_n$ resonances with positive intensity. (b) $\theta = 180°$ spectrum with up/down intensities for the CH_n groups with even/odd parity of n. (c and d) Partially edited spectra containing the C + CH_2 (c) and CH + CH_3 (d) resonances and obtained as the sum and difference, respectively, of the spectra in a and b. The experimental parameters are given in the caption of Figure 7.

HCH_2– (see Coleman et al.[29]), of the *trans*-1,4-CR unit by N, the inverted unit (head–tail) by I, and the *cis*-1,4-CR unit by C. Using this shorthand notation in combination with the liquid-state spectral assignments reported by Coleman et al.,[29] it is possible to identify most of the signals/shoulders listed in Table II to the central unit of various triad sequences (e.g., NNN or NNI). From the assignment in Table II it is concluded that the majority of these

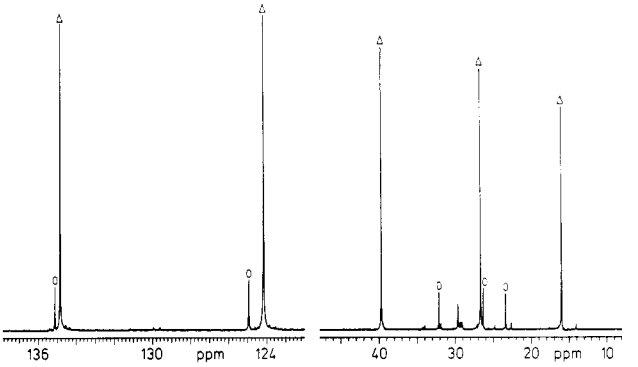

Figure 9. ^{13}C NMR spectrum for a solution of approximately 3% w/w kariten in $CDCl_3$. 256 scans were accumulated with a relaxation time of 4 s. The symbols follow the definitions given for Figure 6.

resonances are caused by *trans*-1,4-CR units in different environments. The weak signal observed in the C + CH_2 spectrum (Figure 3c) at 32.8 ppm can be assigned to the methylene C_γ carbon of a *cis*-1,4-CR unit linked to two N *trans*-1,4-CR units in a head-to-tail configuration. The presence of a small amount of the *cis*-1,4-CR isomer (approximately 5–10%) is also supported by the C_α (quaternary) and C_β signals of this monomer observed as shoulders at 134.4 and 127.1 ppm in the C + CH_2 and CH + CH_3 spectra, respectively. Within the limit of the signal-to-noise ratio the spectra do not show signals from 1,2- or 3,4-CR units. In addition to the signals assigned above, the spectra contain a few weak resonances (Table II) of which the CH_2 signal at 30.5 ppm and the CH signal at 32.6 ppm should be particularly noted. The latter is unambiguously discriminated from the 32.8 ppm C_γ carbon of *cis*-1,4-CR by the editing experiment.

The distribution of the different molecular configurations of the CR monomeric units estimated from the spectra is in accordance with typical compositions of commercial neoprene rubber.[30] It should be noted, however, that the degree of crystallinity in the sample depends on the amount of *trans*-1,4-CR[30] and that the MAS SEMUT spectra solely contain contributions from the noncrystalline parts of the sample. The existence of carbons residing in less mobile (crystalline) environments becomes plausible by comparison of the spectra in parts a and b of Figure 3 which show a noticeable attenuation of signals from protonated carbons in the MAS SEMUT spectra. This observation may be ascribed to dipolar dephasing (or T_2 relaxation) for the crystalline regions during the spin-echo period. This conclusion is supported by CP/MAS experiments (not shown) for our sample which show considerable polarization transfer and thereby the presence of dipolar-coupled carbons. Therefore, with an unknown fraction of the sample in an immobile/crystalline phase, accurate measurement of the *cis*-1,4-CR versus *trans*-1,4-CR ratio is not possible from the present experiments.

C. Ethylene–Propylene Rubber (EPR). Figure 4 illustrates the standard ^{13}C MAS (Figure 4a) and MAS SEMUT (Figure 4b–d) spectra of EPR. The standard MAS and $\theta = 0°$ MAS SEMUT spectra both include carbon resonances from the highly mobile (amorphous) phase; however, some broad components (less mobile part) of the resonances in Figure 4a appear with reduced intensity in the MAS SEMUT spectrum (Figure 4b). The partially edited MAS SEMUT spectra resulting from the $\theta = 0°$ and 180° subexperiments discriminate between CH_2 (Figure 4c) and CH + CH_3 (Figure 4d) resonances. Careful inspection of the spectra in parts a and b of Figure 4 permits identification of 14 more or less well-resolved resonances

Table II
Chemical Shifts, Multiplicities, and Assignment of ^{13}C Resonances for the Six Solid Elastomers[a]

NMR		CR		EPR		SBR		tire rubber		kariten	
δ	assignment[b]	δ	assignment[b,c]	δ	assignment[d]	δ	assignment[e]	δ	assignment[b,f]	δ	assignment[b]
135.4[s]	C_α-*cis*-1,4I	135.6[s]	C_α-NNN-1,4C	46.1[t]	$S_{\alpha\alpha}$	145.7[s]	*S*(Ph-C_1)	145.7	Ph-C_1-S	135.7[s]	C_α-*α-trans*-1,4I
125.9[d]	C_β-*cis*-1,4I	134.6[s]	C_α-NNI-1,4C	39.1[t]	$S_{\alpha\gamma}$	143.0[d]	*v*	143.1[d]	CH-1,2B	135.4[s]	C_α-*cis*-1,4I
33.0[t]	C_γ-*cis*-1,4I	134.4[s]	C_α-NCN-1,4C	38.2[t]	$S_{\alpha\delta}$	131.9[d]	*t*S, *t*v, cS, cv	135.4[s]	C_α-*cis*-1,4I	135.1[s]	C_α-*trans*-1,4I
27.3[t]	C_δ-*cis*-1,4I	134.2[s]	C_α-NIN-1,4C	35.4[t]	$S_{\alpha\beta}$	130.9[d]	*tt*, *tt*, *tc*, *ct*	132.1		131.1[s]	
24.1[q]	C_ϵ-*cis*-1,4I	127.1[d]	C_β-NCN-1,4C	33.7[d]	$T_{\gamma\gamma}$, $T_{\gamma\delta}$, $T_{\delta\delta}$	130.1[d]	*ct*, *tc*, *cc*, *cc*	130.9[d]	C_α-*trans*-1,4B	130.5[d]	
		126.3[d]	C_β-NIN-1,4C	31.1[d]	$T_{\beta\gamma}$, $T_{\beta\delta}$	128.9[d]	*S*(Ph-$C_{2,6}$)	130.2[d]	C_α-*cis*-1,4B	130.3[d]	
		125.4[d]	C_β-NNI-1,4C	30.8[t]	$S_{\gamma\gamma}$, $S_{\gamma\delta}$, $S_{\delta\delta}$	128.3[d]	*S*(Ph-$C_{3,6}$)	128.9	Ph-C_{2-6}-S	125.9[d]	C_β-*cis*-1,4I
		124.7[d]	C_β-NNN-1,4C	28.5[d]	$T_{\beta\beta}$	126.6[d]	*S*(Ph-C_4), *St*, Sc, *vt*, vc	125.9[d]	C_β-*cis*-1,4I	125.1[d]	C_β-*trans*-1,4I
		39.0[t]	C_γ-NNN-1,4C	28.2[t]	$S_{\beta\gamma}$, $S_{\beta\delta}$	115.1[t]	*v*	115.2	CH_2-1,2B	121.4	C_β-*α-trans*-1,4I
		38.6[t]	C_γ-NIN-1,4C	25.5[t]	$S_{\beta\beta}$	48.0[t]		46.5	CH-S	40.6[t]	C_γ-*trans*-1,4I
		32.8[t]	C_γ-NCN-1,4C	23.7[t]		46.4[d]	*t*S, cS	44.1[d]	CH_2-1,2B	39.4[t]	C_γ-*α-trans*-1,4I
		32.6[d]		21.4[q]	$P_{\beta\beta}$	44.1[d]	*tv*, *cv*	33.5[t]	C_β-*trans*-1,4B	34.7[t]	
		30.5[t]		20.7[q]	$P_{\beta\gamma}$, $P_{\beta\delta}$, $P_{\gamma\gamma}$	41.9[t]	*SS*, *vv*	33.1[t]	C_γ-*cis*-1,4I	34.4[t]	
		28.4[t]	C_δ-NNI,NIN-1,4C	15.1[q]		41.1[t]	*t*S, *SS*, v*S*	30.5[t]		33.0[t]	C_γ-*cis*-1,4I
		28.2[t]	C_δ-NNI,NIN-1,4C			39.0[t]	*tv*, *vv*, S*v*	28.2[t]	C_β-*cis*-1,4B	32.8[t]	
		27.5[t]	C_δ-NNN,NCN-1,4C			36.5[t]	*St*, *Sc*, *cv*	27.3[t]	C_γ-*cis*-1,4I	30.6[t]	
		23.6[t]				34.7[t]	*vt*, *vc*	26.0		30.2[t]	
		20.5				33.5[t]	*tt*, *tt*, *ct*, *tc*	24.2[q]	C_ϵ-*cis*-1,4I	30.0[t]	
		15.0				31.2[t]	S*t*	23.5		28.0[t]	
						30.9[t]	v*t*	20.4		27.5[t]	C_δ-*trans*-1,4I
						28.2[t]	*ct*, *tc*, *cc*, *cc*	16.6[q]		27.3[t]	C_δ-*cis*-1,4I
						25.8[t]	Sc, vc	14.9		25.6[t]	
						24.9[q]				24.1[q]	C_ϵ-*cis*-1,4I
										23.6[t]	
										18.2[q]	C_ϵ-*α-trans*-1,4I
										16.6[q]	C_ϵ-*trans*-1,4I
										14.9[q]	

[a] In ppm relative to external TMS. Superscripts s, d, t, and q denote singlets (C), doublets (CH), triplets (CH_2), and quartets (CH_3), respectively, as determined by editing. [b] C_x ($x = \alpha, \beta, \gamma, \delta, \epsilon$) refers to the structural formulas given in the figures. -1,4I, -1,4C, -1,2B, -1,4B, and -S denote 1,4-polyisoprene, 1,4-polychloroprene, 1,2-polybutadiene, 1,4-polybutadiene, and polystyrene, respectively; *α-trans*-1,4I refers to the *α* conformer of crystalline *trans*-1,4-polyisoprene. [c] C_x-XYZ (X, Y, Z = N, I, or C) refers to the C_x carbon for the central unit of triad sequences (see text). The assignments also apply for reversed sequences with N and I interchanged. [d] The assignments refer to the interpretation and terminology of Cheng[32] (see text). [e] The assignments to diad sequences (units in italics) use the terminology of Katritzky and Weiss.[36] If diad not indicated, the assignment includes all diads. [f] Ph-C_n-S (n = 1–6) refers to the phenyl C_n carbon in SBR (see Figure 6).

and shoulders. Complete assignment of the relatively broad resonances associated with bulk EPR represents a considerable task due to the variety of possible ethylene–propylene connectivities, the propylene tacticity, and the presence of propylene inversion. The assignment of solution-state ^{13}C NMR spectra for EPR has been addressed several times in the literature. In this work we find it relevant to compare the results of our edited spectra for the highly mobile phase of this elastomer with the assignment of the liquid-state spectra reported by Cheng et al.[31-33] For this purpose we employ the terminology of Cheng[32] with T, S, and P denoting CH (tertiary), CH_2 (secondary), and CH_3 (primary) groups, respectively, and the Greek letter subscripts refer to the number of bonds separating the considered ^{13}C and the surrounding CH carbons. The assignment of the EPR resonances is given in Table II. It is noted that the multiplicities of the $^{13}CH_n$ resonances obtained from the edited spectra are consistent with the assignment of Cheng;[32] the minor negative and dispersion-like signals in Figure 4d are the result of J cross-talk.[5]

D. Styrene–Butadiene Rubber (SBR). Figure 5 shows the standard ^{13}C MAS (Figure 5a) and ^{13}C MAS SEMUT (Figure 5b,c) spectra of SBR. The spectra in parts a and b of Figure 5 (MAS SEMUT, $\theta = 0°$) display all $^{13}CH_n$ resonances with positive signal intensities, whereas positive and negative intensities in the MAS SEMUT $\theta = 180°$ spectrum (Figure 5c) discriminate the signals according to n even and n odd, respectively. The high resolution observed in these MAS spectra (as compared to earlier reported solid-state NMR spectra of SBR[34,35]) enables identification of a large number of minor resonances, resulting from a variety of different sequences of monomeric styrene and butadiene units. The resolution of resonances and CH_n multiplicity assignment (n even or odd) from the $\theta = 0°$ and $\theta = 180°$ MAS SEMUT experiments are consistent with the information obtained from a DEPT experiment (not shown) for a solution ($CDCl_3$) of the same sample of SBR. Assignment of the ^{13}C MAS spectrum (Table II), following the MAS SEMUT information, may be completed using the assignment for solution-state spectra of SBR by Katritzky and Weiss.[36] The assignment to diad sequences uses the nomenclature of ref 36 with c, t, v, and S denoting *cis*-1,4-butadiene-, *trans*-1,4-butadiene-, 1,2-butadiene-, and styrene-linked units, respectively, oriented according to the structural formulas in Figure 5. A couple of interesting features should be noted. First, MAS SEMUT noticeably improves the spectral resolution as compared to standard MAS experiments. As for EPR, this may be ascribed to dipolar dephasing or T_2 relaxation of less mobile components during the editing fragment. Second, on basis of relative signal intensities in the standard ^{13}C MAS spectrum the composition of monomeric units in the sample is estimated to be 53% *trans*-1,4-butadiene, 8% *cis*-1,4-butadiene, 12% 1,2-butadiene, and 27% styrene (% w/w). These numbers are in accord with the results from the standard liquid-state ^{13}C NMR spectrum for the SBR sample.

E. Tire Rubber. ^{13}C MAS NMR spectra of a tire rubber are shown in Figure 6 with the standard ^{13}C MAS spectrum in Figure 6a, a $\theta = 0°$ ($\tau = 0$) MAS ESCORT spectrum displaying positive signals from all carbons in Figure 6b, and completely edited CH_3, CH_2, CH, and C MAS ESCORT subspectra in Figure 6c–f. Comparison of the spectra in parts a and b of Figure 6 indicates the presence of dipolar-coupled and/or fast-relaxing constituents from immobile (e.g., cross-linked) regions of the tire rubber since a number of broad resonances (e.g., at 26.0,

30.5, 46.5, 115.2, 128.8, and 145.7 ppm) are considerably attenuated in the MAS ESCORT spectra. The five intense resonances denoted with the symbol ○ in Figure 6a are immediately identified as *cis*-1,4-polyisoprene (the Greek letter symbols in the spectra refer to the corresponding carbons of the structural formula). Among other components in tire rubber, polybutadiene rubber (BR) and styrene–butadiene rubber (SBR) are usually the most predominant. The relevant structural formulas are shown above the spectra. The intense signals at 28.2 and 130.2 ppm are attributed to the CH_2 and the diene CH carbons of *cis*-1,4-polybutadiene (symbol △), while the shoulders at 33.5 and 130.9 ppm are assigned to *trans*-1,4-polybutadiene (symbol ▲).[23,37] Furthermore, the weak peaks observed at 44.1, 115.2, and 143.1 ppm can be assigned to $-CH_2-$, $=CH_2$, and $=CH-$ constituents, respectively, of 1,2-polybutadiene (symbol □). In addition to its contribution to the butadiene peaks, SBR manifests itself by weak resonances for styrene at 46.5, 128.8, and 145.7 ppm (denoted by the symbol ★). These broad signals, which are almost completely suppressed in the MAS ESCORT spectra, are assigned according to the spectrum of SBR in Figure 5. It should be noted that quite large variations in the relative content of *cis*-1,4-polyisoprene, butadiene rubber, and SBR have been observed for different tires investigated in our laboratory.

F. Kariten. As a final and intriguing example of spectral editing for solid elastomers Figure 7 presents ^{13}C MAS SEMUT spectra of the amorphous phase for semicrystalline kariten (a crude mixture identified as mainly *cis*- and *trans*-1,4-polyisoprene and obtained as a residue from production of vegetable oil). Figure 7a shows the standard ^{13}C MAS spectrum, Figure 7b the $\theta = 0°$ MAS SEMUT spectrum, and Figure 7c–f fully edited CH_3, CH_2, CH, and C MAS SEMUT subspectra. The spectra demonstrate that (i) MAS SEMUT is very selective in probing/editing resonances only from the amorphous constituents of this mixture of polyisoprenes and (ii) assignment of the more crowded regions of the spectra is clearly facilitated by editing. From the spectra the two major components can immediately be identified as the cis and the trans isomers of 1,4-polyisoprene (structural formulas are shown above the spectra). The *cis*-1,4-polyisoprene resonances (symbol ○) are easily identified from the spectra of NR in Figure 2. Five of the remaining major resonances (symbol △) can be assigned to amorphous *trans*-1,4-polyisoprene (gutta-percha).[23,38] It appears that resonances at 18.2, 39.4, 121.4, and 135.7 ppm in the standard ^{13}C MAS spectrum are suppressed in the MAS SEMUT spectra. Using this observation and the assignment of Patterson and Koenig,[38] these resonances may be assigned to the methyl C_ϵ (18.2 ppm), the methylene C_γ (39.4 ppm), and the olefinic C_β (121.4 ppm) and C_α (135.7 ppm) carbons for the monoclinic α conformer of crystalline *trans*-1,4-polyisoprene (symbol ▲); we note that the C_δ resonance at 27.0 ppm is not resolved in the Figure 7a spectrum. Apart from these intense signals a number of weak, but well-defined, resonances and shoulders are observed at 14.9 ppm (CH_3), 23.6, 25.6, 28.0, 30.0, 30.2, 30.6, 32.8, 34.4, and 34.7 ppm (CH_2) and 130.3 and 130.5 ppm (CH) (Table II) for our sample of kariten. Again it should be noted that weak (negative, positive, or dispersion-like) signals in the fully edited subspectra of Figure 7 may result from J cross-talk;[5] however, these artifacts are easily identified by comparison of the different spectra.

Comparison of the MAS SEMUT spectra of kariten in parts c–f of Figure 7 with the $\theta = 0°$ spectrum in Figure 7b reveals that complete editing is associated with a substantial loss in signal-to-noise (S/N).[39] In numerous cases, including the polyisoprene samples, where the regions of C (CH) and CH_2 (CH_3) signals are well-separated, partial editing into CH_n subspectra with even and odd parity of n provides the necessary multiplicity information. Even/odd editing can in principle, as demonstrated for solid kariten in Figure 8, be performed without loss in S/N since the $\theta = 0°$ and $\theta = 180°$ spectra ideally contain full intensity for all carbons. It should be noted that the partially edited spectra also enable unambiguous multiplicity assignment of very weak signals, for example, in the region from 130.3 to 131.1 ppm, assignments that are most convincingly obtained from the $\theta = 180°$ spectrum (Figure 8b).

Information about the relative amounts of the cis and trans isomers of 1,4-polyisoprene in our kariten sample and their phase distribution can be obtained by comparing with the standard ^{13}C spectrum in Figure 9 of kariten dissolved in $CDCl_3$. Measurement of relative peak intensities from the liquid-state spectrum (Figure 9) yields a total composition of ca. 15% *cis*-1,4- and 85% *trans*-1,4-polyisoprene. The corresponding measurement for the MAS SEMUT $\theta = 0°$ spectrum, which exclusively displays signals from the amorphous phase, yields a composition of 35% *cis*-1,4- and 65% *trans*-1,4-polyisoprene. In combination, these numbers suggest that about 70% of the *trans*-1,4-polyisoprene occurs in a crystalline state at room temperature. This conclusion is supported by CP/MAS experiments which show intense signals for the α and β conformers of crystalline *trans*-1,4-polyisoprene.

Conclusions

This work demonstrates that spectral editing techniques represent a powerful tool for assignment of ^{13}C resonances associated with the amorphous (mobile) phases of solid elastomers. The combined effect of (i) magic-angle spinning with proton decoupling during data acquisition and (ii) the molecular motions characteristic for the amorphous phase of elastomers allow "liquid-state type" NMR experiments such as spectral editing to be performed for these systems. The MAS SEMUT and MAS ESCORT pulse sequences presented here have been successfully applied to characterize the amorphous phases for a series of single- and multiple-component rubbers at ambient temperature. Applications of the CP/MAS SEMUT technique and/or other spectral editing methods to the crystalline (immobile) phases of polymers are currently in progress.

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