Macromolecules **1995,** *28,* 2009–2015

Strategies for Structural and Quantitative Analysis of Heterogeneous Block Copolymers by ^{13}C MAS NMR Spectroscopy

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Received June 9, 1994; Revised Manuscript Received December 13, 1994[⊗]

ABSTRACT: Strategies for structural and quantitative analysis of unknown heterogeneous block copolymers employing solid-state ^{13}C magic-angle spinning (MAS) NMR techniques are presented. Combinations of standard single-pulse, cross-polarization, cross-polarization–depolarization, and SEMUT spectral editing MAS experiments enable efficient separation, identification, and quantitation of resonances from mobile as well as immobile phase constituents of heterogeneous polymers. The utility of these techniques for structural and quantitative analysis of complex polymers is demonstrated for three block copolymers, initially of unknown structure and composition. The three samples investigated here have been identified as polypropylene/polyethylene/ethylene–propene–diene rubber (PP/PE/EPDM), polyethylene/ethylene–propene rubber (PE/EPR), and polystyrene/polyethylene/butadiene rubber (PS/PE/BR).

Introduction

Characterization of heterogeneous block copolymers of unknown composition and unknown structures of the polymer constituents represents a difficult challenge to the analytical chemist. This is especially true if the goal involves determination of the structures of the individual polymers along with a quantitative assessment. The difficulties encountered are caused by a number of factors including (i) the presence of crystalline, semicrystalline, and/or amorphous phases of different mobilities within the block copolymer and (ii) variation of the chain lengths and tacticities of monomers in the repeat units of the different polymers within these phases. To our knowledge no examples of a detailed characterization in terms of structure and quantitative analysis have been reported for heterogeneous block copolymers of unknown (or partially unknown) composition and structure for the polymer constituents. This work reports strategies for such analysis of block copolymers using new and established methods based on the techniques of high-resolution solid-state ^{13}C magic-angle spinning (MAS) NMR spectroscopy.

^{13}C MAS NMR has become an important tool for characterization of polymers and elastomers in bulk due to its ability to provide structural and quantitative information about amorphous as well as crystalline materials.[1–3] Using pulse methods based on MAS[4,5] and high-power ^{1}H decoupling or on the well-established combination[6] of these techniques with cross-polarization (CP),[7] high-resolution solid-state ^{13}C NMR spectra of polymers are routinely obtained. Thereby, ^{13}C MAS NMR may provide information about composition, chain structures, tacticities, monomer sequence distributions, phase properties, and dynamics of polymer chain segments. However, for complex heterogeneous block copolymers direct access to this information is often severely hampered because the ^{13}C MAS spectra are complicated by overlap of resonances from different polymer structures and phase components. Thus, assignment of the ^{13}C MAS spectra in terms of structural components and a subsequent quantitative analysis would benefit from techniques which enable separation of signals according to mobility and/or structure.

Recently developed solid-state NMR spectral editing techniques in our laboratory[8,9] serve as an aid for a large part of the needs described above. Of these techniques MAS SEMUT[8] allows separation and identification of resonances from *mobile* ^{13}C atoms according to the number of directly bonded protons (referred to as spectral editing) while efficiently suppressing resonances from *immobile* constituents. Another method, referred to as cross-polarization–depolarization (CPD) MAS editing,[9] enables spectral editing for *immobile* constituents. Furthermore, it is noted that the CPD/MAS technique[9–14] also allows distinction of resonances from mobile and immobile constituents in semicrystalline solids.[14] Thus, in relation to heterogeneous block copolymers these techniques represent a clue to (i) selective detection of resonances belonging to either mobile[8] or immobile[9] phases along with (ii) a separation and identification of the ^{13}C resonances within these phases according to the numbers of directly bonded protons. Thereby an unambiguous assignment of resonances and identification of the polymeric constituents within the block copolymer should be possible. Quantitative assessment of the polymers within the mobile and immobile phases may then be established from a standard ^{13}C single-pulse MAS experiment using a sufficiently long relaxation delay in order to ensure quantitatively reliable signal intensities.

This work illustrates the strategies used, employing the single-pulse, CP, CPD, and SEMUT MAS experiments, to efficiently discriminate, assign, identify, and quantify ^{13}C MAS NMR spectra for both mobile and immobile domains of complex semicrystalline polymers, copolymers, or polymer blends. We have explored the utility of the techniques for analysis of three heterogeneous block copolymers, initially of unknown (or partially unknown) structure and composition, however, identified during the course of this work as PP/PE/EPDM (polypropylene/polyethylene/ethylene–propene–diene monomer), PE/EPR (polyethylene/ethylene–propene rubber), and PS/PE/BR (polystyrene/polyethylene/butadiene rubber).

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

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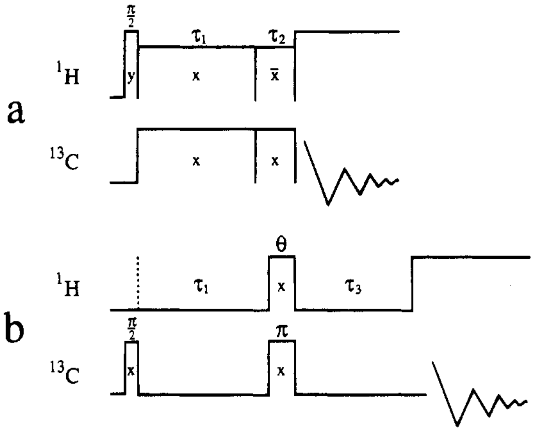


Figure 1. Pulse schemes for the solid-state NMR techniques (a) CPD/MAS and (b) MAS SEMUT employed in this study for analysis of block copolymers.

Experimental Section

A. Samples. Three block copolymers (**1**, **2**, and **3**), from different production lines of unknown origin, were received from various industrial users of polymer materials. Sample **1**, a block copolymer used for bumpers in the car industry, was suspected by the user to be a physical mixture of approximately 20% w/w EPDM rubber and 80% w/w block copolymer of isotactic polypropylene (PP) and polyethylene (PE). The EPDM, an amorphous terpolymer of ethylene, propylene, and a diene, was claimed to contain approximately 5% w/w diene of unknown structure; both structure and quantitation of the diene were determined here (*vide infra*). No information regarding application, structure, and composition was available for samples **2** and **3**; however, during the course of this study they were identified as PE/EPR (**2**) and PS/PE/BR (**3**) copolymers and their composition was determined. The three samples were used as received and were cut into small pieces before being packed into the MAS rotor.

B. Instrumentation and Experimental Techniques. Natural-abundance ^{13}C MAS spectra were recorded on a Varian XL-300 (7.05-T) spectrometer at 75.43 MHz. All experiments were performed at ambient temperature (ca. 25 °C) employing a home-built high-speed spinning CP/MAS probe[15] with 7-mm PSZ rotors (partially stabilized zirconia; 220-μL sample volume). Spinning speeds in the range of $\nu_r \approx$ 3.5–6.3 kHz were used along with radio-frequency (rf) field strengths ($\gamma B_1/2\pi$) of ca. 40 kHz for spin-lock (CP and CPD) and ca. 65 kHz for ^{1}H-decoupling. The rf field strengths used for the ^{1}H/^{13}C pulses and CP spin-lock (exact Hartmann–Hahn match) were carefully calibrated.[16] All single-pulse ^{13}C MAS experiments used a pulse width of 4 μs, corresponding to a flip angle of 55°. Relaxation delays between 1 and 160 s were employed. For each sample a series of single-pulse ^{13}C MAS spectra with different relaxation delays were recorded to ensure quantitatively reliable signal intensities for the spectra obtained with the longest relaxation delays. The magic angle was adjusted by minimizing the line width of the spinning sidebands for the satellite transitions in the ^{23}Na MAS NMR spectrum of $NaNO_3$.[17] ^{13}C chemical shifts are in ppm relative to external TMS.

Standard single-pulse, CP (Figure 1a, $\tau_2 = 0$), CPD (Figure 1a, $\tau_2 \neq 0$), and SEMUT (Figure 1b) MAS pulse sequences were applied. The CP and CPD experiments used spin-lock periods (τ_1) for cross-polarization in the range of 100–2500 μs. The CPD experiments used subsequent cross-depolarization periods (τ_2) between 10 and 100 μs with the phase of the ^{1}H spin-lock rf field being inverted relative to the phase used during τ_1. The MAS SEMUT experiments employed flip angles θ = 0 and 180° for the editing pulse in order to discriminate ^{13}C resonances from the CH_n (n = 0, 1, 2, and 3) spin systems according to n-even and n-odd parity for the number of attached protons. Due to the $\cos^n \theta$ dependence for the SEMUT intensities, parity editing is accomplished by linear combination of the $\theta = 0°$ (positive intensities for all ^{13}C) and $\theta = 180°$ (positive and negative intensities for n even and odd, respectively) MAS SEMUT subspectra. The SEMUT spin-echo periods were adjusted to heteronuclear J couplings in the range $J_{\min}$ = 120 Hz to $J_{\max}$ = 150 Hz using $\tau_1 = \{2[J_{\min} + 0.146(J_{\max} - J_{\min})]\}^{-1}$ and $\tau_3 = \{2[J_{\min} - 0.146(J_{\max} - J_{\min})]\}^{-1}$.[8,18,19] We note that long τ_1 and τ_3 periods (i.e., ms range) in the MAS SEMUT pulse sequence cause efficient ^{1}H–^{13}C dipolar dephasing and transverse relaxation of rigid carbons, implying that highly mobile carbons only are selectively probed.[8]

Following resolution and assignment of all ^{13}C resonances to the various structure and phase components, quantitative assessments of these constituents were accomplished using computer deconvolution of the fully relaxed single-pulse ^{13}C MAS spectra. Fitting of the experimental spectra was performed on a SUN Sparc-10/51 workstation using the deconvolution procedure of the Varian VNMR software.

Results and Discussion

The utility of the proposed strategies, employing combinations of single-pulse, CP, CPD, and SEMUT ^{13}C MAS experiments, for structural and quantitative analysis of unknown heterogeneous block copolymers is demonstrated experimentally for samples **1**, **2**, and **3** in Figures 2–5. The resulting ^{13}C chemical shifts, even/odd parities for the number (n) of protons in the CH_n groups, and assignments to the monomeric units of the polymer chains are summarized in Table 1. Quantitative results including mole fractions of monomeric units in the various identified polymer components and weight fractions of the polymers constituting the three block copolymers are summarized in Table 2. Applications of the combined techniques are outlined and discussed in detail for sample **1** and subsequently treated more briefly for samples **2** and **3**.

A. Sample 1 (PP/PE/EPDM). Single-pulse ^{13}C MAS spectra of sample 1 recorded with recycle times of 1, 8, and 60 s are shown on the same absolute intensity scale in parts a, b, and c of Figure 2, respectively. Clearly, overlap from the rather broad resonances complicates an unambiguous interpretation of these spectra in terms of structure, composition, and/or sequences of monomer units for the different phases. However, differentiation between the ^{13}C resonances from mobile and immobile components may partly be conducted by comparison of the three single-pulse ^{13}C MAS spectra. The fast repetition rate employed for Figure 2a favors detection of resonances originating from mobile components with short ^{13}C spin–lattice relaxation times (T_1), while resonances from more rigid carbons (e.g., crystalline regions) are attenuated due to their significantly longer T_1's. The 8-s recycle delay ensures sufficient relaxation so that resonances from *both* mobile and immobile domains are clearly observed. Finally, the spectrum recorded in Figure 2c (pulse flip angle of 55° and a recycle time of 60 s) allows for complete relaxation of resonances from *both* mobile and immobile components and therefore reflects more reliably the quantitative composition of the block copolymer.

Comparison of parts a, b, and c of Figure 2 reveals that the intense resonances at 26.5 and 44.2 ppm in Figure 2c increase noticeably by increasing the recycle time. This supports assignment of these resonances to the CH and CH_2 groups, respectively, of polypropylene (PP) in the immobile block copolymer, in agreement with the results for isotactic PP by Bunn et al.[20,21] Similarly, in accordance with these authors the broad resonance observed at 22.2 ppm is assigned to the CH_3 group of isotactic PP. Assisted by the findings in a previous MAS

Table 1. Chemical Shifts, Proton Parities, and Assignments of ^{13}C Resonances for Sample 1 (PP/PE/EPDM), 2 (PE/EPR), and 3 (PS/PE/BR) Block Copolymers[a]

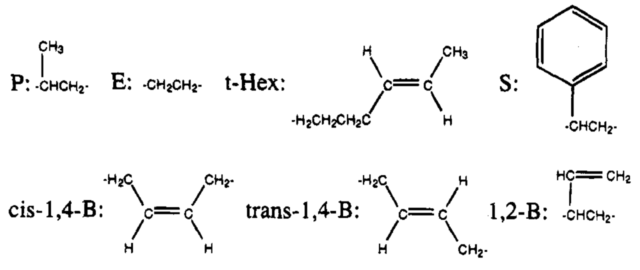
1 PP/PE/EPDM			2 PE/EPR			3 PS/PE/BR			
	assignment			assignment			assignment		
δ (ppm)	PP/PE	EPDM[c,d]	δ (ppm)	PE	EPR[c]	δ (ppm)	PS[b,e]	PE	BR[c,f]
130.6^o		–CH= t-Hex	169.8^e			146.5	S(Ph-C_1)		
126.3^o		–CH= t-Hex	73.9^o			143.1^o			ν (all diads)
46.1^e		$S_{\alpha\alpha}$	38.1^e		$S_{\alpha\delta}$, $S_{\alpha\gamma}$	130.7^o			*t*t, t*t*, *t*c, c*t*
44.2	–CH_2– PP[b]		35.3^e		$S_{\alpha\beta}$	130.2^o			*c*t, t*c*, *c*c, c*c*
38.3^e		$S_{\alpha\gamma}$	33.6^o		$T_{\gamma\gamma}$, $T_{\delta\delta}$, $T_{\gamma\delta}$	128.5	S(Ph-$C_{2,6}$)		
38.1^e		$S_{\alpha\delta}$	33.0	–CH_2– PE[b]		127.0	S(Ph-$C_{3,5}$)		
35.1^e		$S_{\alpha\beta}$	30.8^e	–CH_2– PE[c]	$S_{\gamma\gamma}$, $S_{\delta\delta}$, $S_{\gamma\delta}$	126.3	S(Ph-C_4)		
33.7^o		$T_{\gamma\gamma}$, $T_{\delta\delta}$, $T_{\gamma\delta}$	28.0^e		$S_{\beta\gamma}$, $S_{\beta\delta}$	115.1^e			ν (all diads)
32.9	–CH_2– PE[b]		26.2^e			46.1	S(CH)		
31.1^o		$T_{\beta\gamma}$, $T_{\beta\delta}$	25.5^e		$S_{\beta\beta}$	44.3^o			t*ν*, c*ν*
30.9^e	–CH_2– PE[c]	$S_{\gamma\gamma}$, $S_{\delta\delta}$, $S_{\gamma\delta}$	24.1^e			40.8	S(CH_2)		
28.5^o		$T_{\beta\beta}$	23.6^e			39.0^e			*t*v
28.2^e		$S_{\beta\gamma}$, $S_{\beta\delta}$	21.3^o		$P_{\beta\beta}$	34.9^e			*ν*t, *ν*c
26.5	>CH PP[b]		20.6^o		$P_{\beta\gamma}$, $P_{\beta\delta}$, $P_{\gamma\gamma}$	33.5^e			*t*t, t*t*, *t*c, c*t*
25.5^e		$S_{\beta\beta}$	14.7^o			32.9		–CH_2– PE[b]	
22.2	–CH_3 PP[b]					31.0^e		–CH_2– PE[c]	
22.1^o						28.3^e			*c*t, t*c*, *c*c, c*c*
21.4^o		$P_{\beta\beta}$				25.8^e			*c*v
20.7^o		$P_{\beta\gamma}$, $P_{\beta\delta}$, $P_{\gamma\gamma}$							
18.8^o		–CH_3 t-Hex							

[a] In ppm relative to external tetramethylsilane (TMS). Superscripts o and e denote CH_n carbons with n even and n odd parity, respectively, of the number of protons as determined by MAS SEMUT editing. [b] Immobile (crystalline) phase. [c] Mobile (amorphous) phase. [d] The nomenclature is adopted from Cheng.[31] t-Hex denotes the *trans*-1,4-hexadiene monomer. [e] S(Ph-C_n) refers to the phenyl C_n carbon in PS. [f] The assignment to diad sequence (unit in italics) uses the terminology of Katritzky and Weiss.[35]

Table 2. Composition of Sample 1 (PP/PE/EPDM), 2 (PE/EPR), and 3 (PS/PE/BR) Block Copolymers Determined by ^{13}C MAS NMR

copolymer	polymer	weight %	monomeric unit[a]	mole %
	PP	52		
	PE	8		
1: PP/PE/EPDM			E	67
	EPDM	40	P	23
			t-Hex	10
	PE	35		
2: PE/EPR	EPR	65	E	84
			P	16
	PS	35		
	PE	37		
3: PS/PE/BR			*cis*-1,4-B	59
	BR	28	*trans*-1,4-B	35
			1,2-B	6

[a] Monomeric units:



SEMUT study of EPR,[8] the resonances at 20.7, 25.5, 28.2, 30.9, 33.7, and 46.1 ppm are assigned to ethylene and propene components of a mobile EPDM terpolymer. The presence of a diene within the flexible copolymer is concluded from the resonances observed at 18.8, 126.3, and 130.6 ppm. Using standard additivity rules for chemical-shift calculations in alkenes[22] and comparison with a liquid-state NMR study of EPR and EPDM by van der Velden,[23] these resonances can be assigned to the CH_3 (calculated 17.9 ppm) and two CH diene carbons (calculated 125.7 and 131.7 ppm) of *trans*-1,4-hexadiene being incorporated into the EPDM via the 1,2-double bond.

A somewhat unusual feature is observed for the PP methyl resonance at 22.2 ppm in Figure 2a–c in that its intensity decreases noticeably by increasing the relaxation delay, in particular from 1 to 8 s (Figure 2a to 2b). This feature is also observed for the EPDM methylene resonance at 30.9 ppm and to a smaller degree for the two overlapping EPDM CH_2 resonances at 38.2 ppm. To further investigate this observation several experiments using different gated ^{1}H-decoupling schemes and variable-temperature ^{13}C MAS NMR were performed. These experiments show that the increased signal intensities observed for short relaxation delays are caused by nuclear Overhauser enhancement[24,25] induced by the ^{1}H-decoupling applied during acquisition (80 ms) provided the delay is comparable to and not much longer than $T_1(^{13}C)$.[26,27] For the two above-mentioned signals, $T_1(^{13}C)$ was determined to be 0.7 s (22.2 ppm) and 0.3 s (30.9 ppm). We note that ^{13}C single-pulse experiments with fast repetition rates for a sample of ethylene–propylene rubber (EPR) show similar behavior for the 30.8 ppm methylene signal (not shown).

Overall, the three single-pulse ^{13}C MAS spectra in Figure 2a–c allow resolution of a total of 14 resonances (including shoulders). It is evident, however, that even assisted by the different combinations of signals from the mobile and immobile phases obtained for the various relaxation delays, the observation of all resonances could be hampered by overlap of resonances in the aliphatic region. ^{13}C CP/MAS experiments with *short* (<100 μs) CP spin-lock periods τ_1 (Figure 1a, $\tau_2 = 0$) preferentially probe CH_n carbons from crystalline and/or highly immobile polymer regions and therefore represent an alternative means to distinguish ^{13}C resonances from the two phases in the block copolymer. This is demonstrated in parts d and e of Figure 2 which show ^{13}C CP/MAS spectra employing τ_1 values of 2500 and 100 μs, respectively. While the spectrum in Figure

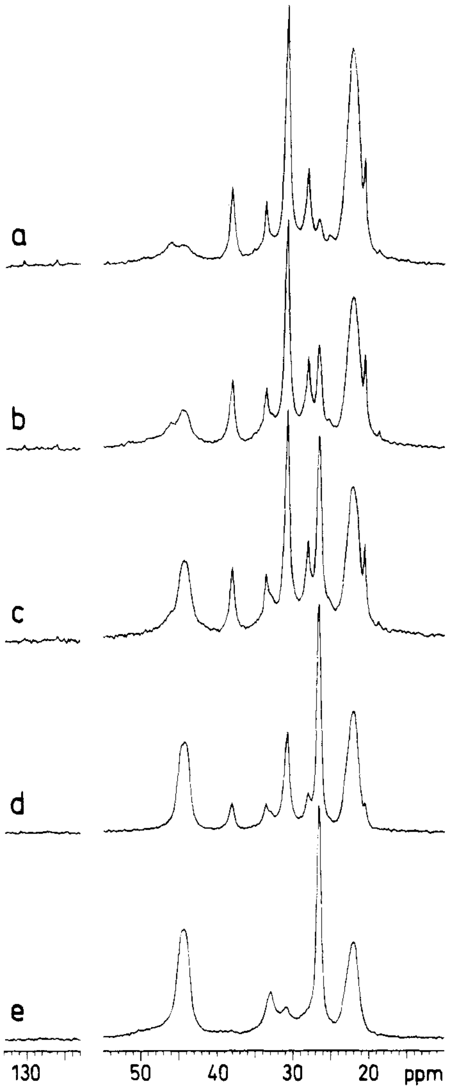


Figure 2. ^{13}C MAS and CP/MAS spectra of sample **1** (PP/PE/EPDM block copolymer): (a−c) ^{13}C MAS single-pulse excitation spectra (ν_r = 6216 Hz) with relaxation delays of (a) 1, (b) 8, and (c) 60 s; (d,e) ^{13}C CP/MAS spectra recorded using contact times τ_1 of (d) 2500 and (e) 100 μs and a relaxation delay of 4 s ($\tau_2 = 0$, ν_r = 6216 Hz).

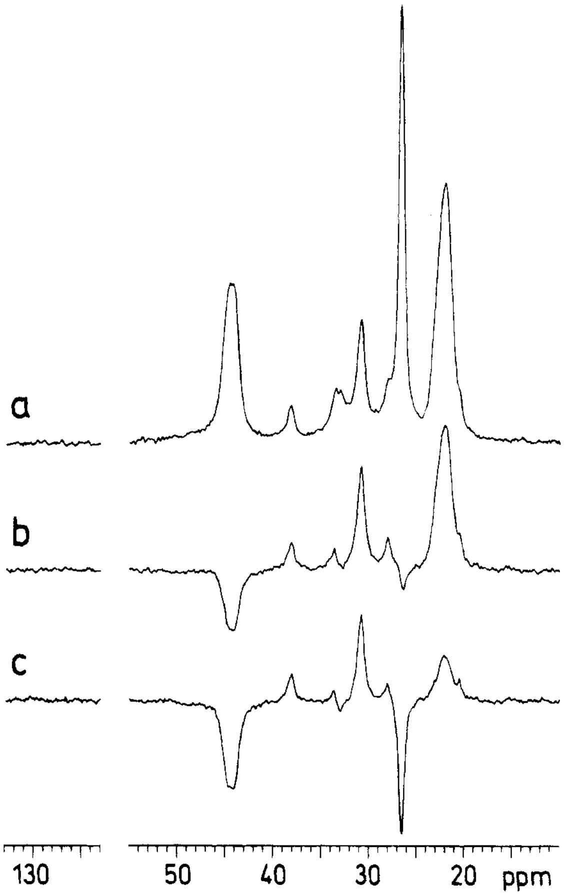


Figure 3. ^{13}C CPD/MAS spectra (ν_r = 6351 Hz, a relaxation delay of 8 s, and 320 scans) of sample **1** (PP/PE/EPDM) obtained using τ_1 = 2000 μs and depolarization periods τ_2 of (a) 10, (b) 50, and (c) 100 μs.

2d exhibits resonances from *both* the mobile and immobile components (although dominated by the latter), the spectrum in Figure 2e almost exclusively displays resonances from the immobile regions of the block copolymer (i.e., from carbons with the strongest ^{13}C−^{1}H dipolar couplings). Apart from a confirmation of the assignment for the PP carbons given above, Figure 2e shows an additional quite intense and well-resolved resonance at 32.9 ppm which may be assigned to crystalline polyethylene (PE)[28] in the rigid block copolymer matrix.

Alternatively, an efficient separation of resonances associated with different phase constituents may be achieved using the cross-polarization−depolarization (CPD) experiment,[9−14] which has proven useful for separation of resonances from mobile and immobile carbons[14] and in spectral editing of ^{13}C CP/MAS spectra for rigid solids.[9] CPD distinguishes ^{13}C resonances from morphologically different polymer regions according to their different ^{1}H−^{13}C CP behavior. Within the conventional "I−S reservoir" thermodynamic model,[7,29] this feature follows from the relationship $I(\tau_1,\tau_2) \propto [2\exp\{-\tau_1/T_{\mathrm{CH}}\} - \exp\{-(\tau_1 + \tau_2)/T_{\mathrm{CH}}\} - 1]$ between the signal intensity $I(\tau_1,\tau_2)$ and the cross-relaxation time T_{CH}, the CP period τ_1, and the depolarization period τ_2.[10] During the relatively long τ_1 period all ^{13}C resonances are excited to some positive signal intensities, which during the subsequent τ_2 period depolarize with a rate highly dependent on T_{CH}. Rigid carbons depolarize rapidly, resulting in zero-crossings of the signal intensities for small τ_2 values, whereas the zero-crossings for mobile carbons occur for significantly longer τ_2 values. Figure 3 shows CPD/MAS spectra of sample **1** recorded using τ_1 = 2000 μs (ensures efficient excitation for both phases) and τ_2 depolariztion periods of 10 (Figure 3a), 50 (Figure 3b), and 100 μs (Figure 3c). The spectrum in Figure 3a is essentially that of a CP/MAS experiment with a long CP time (Figure 2d), whereas the admixture of positive and negative signals in Figure 2b,c reveals significant variations in T_{CH} for the different carbons. The 26.5 and 44.2 ppm resonances from crystalline PP and the 32.9 ppm resonance from crystalline PE undergo the fastest depolarization and all exhibit negative signal intensities for τ_2 = 50−100 μs (e.g., Figure 3c). A somewhat slower depolarization is observed for the PP CH_3 signal at 22.2 ppm, which appears with positive, however, strongly attenuated intensity in Figure 3c along with the almost unaffected resonances for the mobile carbons of the EPDM polymer.

MAS SEMUT represents an extremely useful technique for examination of the amorphous/mobile phases in semicrystalline polymers[8] because (i) the ^{13}C spectra contain signals exclusively from the mobile phase, (ii) the spectra are generally of considerably better resolution than a standard single-pulse ^{13}C MAS spectrum

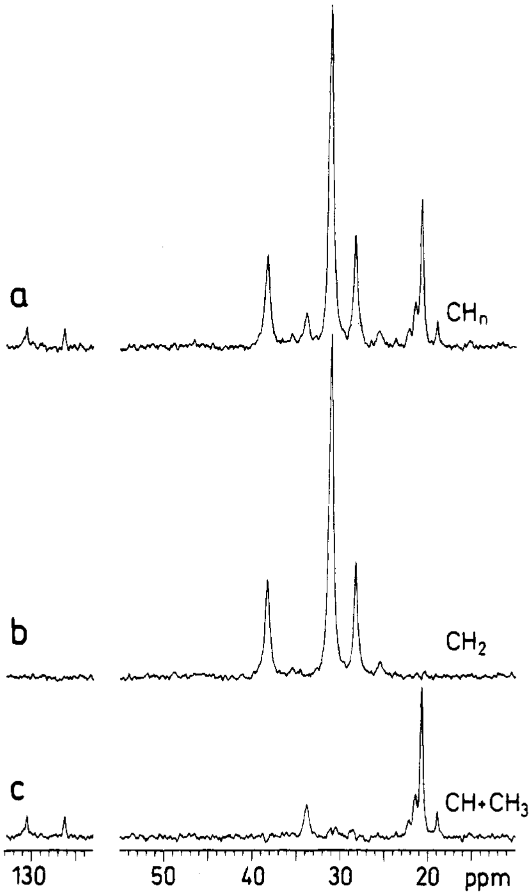


Figure 4. ^{13}C MAS SEMUT spectra (ν_r = 3512 Hz, a relaxation delay of 4 s, and 8192 scans for each of the $\theta = 0$ and 180° subexperiments) of sample **1** (PP/PE/EPDM) showing resonances from the mobile EPDM terpolymer exclusively. Spectrum a contains resonances from all carbons (CH$_n$) whereas spectra b and c show CH$_n$ signals edited according to n even (CH$_2$) and odd (CH + CH$_3$), respectively.

since broad and fast-relaxing signals from immobile and interfacial regions are suppressed, and (iii) each ^{13}CH$_n$ signal is labeled according to its proton multiplicity n, facilitating assignment of the resonances in terms of molecular structure. The suppression of signals from the immobile regions of the sample and the improved resolution of the ^{13}C MAS SEMUT spectra become evident by comparison of the all-carbon (CH$_n$) $\theta = 0°$ MAS SEMUT spectrum of sample **1** in Figure 4a with the ^{13}C MAS spectra in Figure 2. In particular, one should note the efficient suppression of the broad CH$_3$ resonance from PP observed at 22.2 ppm in Figure 2. The MAS SEMUT spectrum (Figure 4a) enables detection of three additional and well-resolved CH$_3$ resonances at 20.7, 21.4, and 22.1 ppm from the mobile EPDM terpolymer which could not be observed in the standard ^{13}C MAS spectra. Resonances at similar positions have recently been observed in ^{13}C MAS SEMUT spectra of EPR.[8] Furthermore, the 18.8 ppm resonance from the CH$_3$ group of the *trans*-1,4-hexadiene unit of EPDM is clearly resolved. Finally, the spectral editing into CH$_n$ subspectra with n even (CH$_2$, Figure 4b) and n odd (CH + CH$_3$, Figure 4c) supports assignment of the diene signals to $-$CH$=$CH$-$ carbons and clearly distinguishes the CH$_3$ and CH (33.7 ppm) resonances from the methylene resonances.

Assisted by the spectral editing, the liquid-state NMR assignments of EPR by Cheng et al.,[30-32] and a recent ^{13}C MAS SEMUT study of EPR,[8] the ^{13}C resonances in the spectral region from 20.7 to 46.1 ppm can be assigned to the various methyl (P), methylene (S), and methine (T) carbons from the ethylene and propene monomeric units in EPDM. It is noted that interpretation of the spectra is generally complicated by the large number of resonances due to a variety of ethylene–propylene connectivities, propylene tacticities, and propylene inversions. The assignment employs the terminology of Cheng[31] and is given in Table 1 along with assignments for the diene constituent in EPDM and the rigid PP and PE phases of the block copolymer. Using the methylene signal intensities[30] from the ^{13}C MAS (Figure 2c) and MAS SEMUT (Figure 4b) spectra, the composition of the flexible EPDM terpolymer is found to be 67 ± 5% ethylene, 23 ± 5% propylene, and 10 ± 5% *trans*-1,4-hexadiene (mole fractions). Based on this composition of EPDM and the relative signal intensities in the ^{13}C MAS spectrum of Figure 2c, we determine the PP/PE/EPDM copolymer to be a mixture of 52 ± 5% w/w PP, 8 ± 5% w/w PE, and 40 ± 5% w/w EPDM. It is noted that the above fraction of PE only includes crystalline components since it is impossible to discriminate the S_{xy} ($x,y = \gamma,\delta$) CH$_2$ resonances from EPDM from potential CH$_2$ resonances from amorphous PE. Thus, potential contributions from amorphous PE are included in the numbers of EPDM.

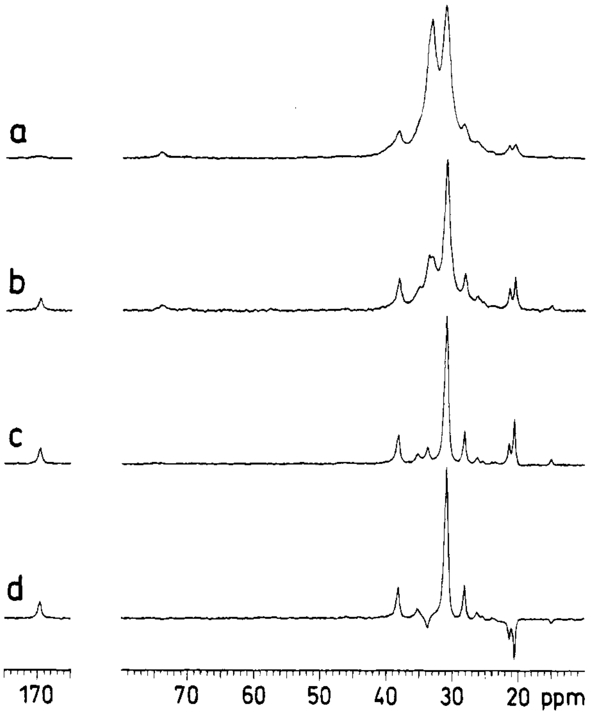


Figure 5. ^{13}C CP/MAS, MAS, and MAS SEMUT spectra (ν_r = 5152 Hz) of sample **2** (PE/EPR block copolymer): (a) CP/MAS spectrum (τ_1 = 800 μs, 144 scans, and a relaxation delay of 4 s); (b) MAS spectrum (256 scans and a relaxation delay of 60 s); (c,d) MAS SEMUT spectra recorded using (c) $\theta = 0°$ and (d) $\theta = 180°$.

B. Sample 2 (PE/EPR). ^{13}C MAS spectra of sample **2** are shown in Figure 5. The CP/MAS (Figure 5a) and MAS (Figure 5b) spectra, recorded using 4- and 60-s relaxation delays, respectively, indicate the presence of constituents with different mobilities in this sample. In particular, the resonance at 32.9 ppm is markedly influenced by the different excitation conditions and has been ascribed to crystalline PE, which appears to be present in quite high quantities for this polymeric material. PE is a semicrystalline polymer and its ^{13}C MAS NMR spectra are usually associated with a second and relatively broader resonance at ca. 31.0 ppm from the amorphous phase. This resonance is not clearly resolved in the ^{13}C MAS spectrum (Figure 5b), but most likely it contributes to the line-broadening observed near the baseline at this resonance position.

Assignment of the rather crowded aliphatic region of the ^{13}C MAS spectrum is greatly facilitated by using MAS SEMUT as illustrated by the spectra in Figure 5c,d. The two MAS SEMUT spectra contain ^{13}C resonances for the amorphous copolymer exclusively, with positive signal intensities for all carbons in Figure 5c ($\theta = 0^\circ$) and positive/negative intensities for CH_n groups with n-even/n-odd proton parity in Figure 5d ($\theta = 180^\circ$). The noticeably improved resolution, suppression of resonances from immobile and interfacial components (especially crystalline PE), and labeling of the ^{13}C resonances according to the number of attached protons enable identification and unambiguous assignment of nearly all resonances in the spectral region from 20 to 40 ppm to an EPR elastomer (cf. the spectra in Figure 4). The assignment and chemical shifts are summarized in Table 1. Based on the intensities of the methylene resonances in the MAS SEMUT $\theta = 0^\circ$ spectrum (on the assumption of essentially equal transverse relaxation among the backbone methylene carbons) and deconvolution of the ^{13}C MAS spectrum in Figure 5b (using line positions and widths for the mobile components taken from the MAS SEMUT spectra), the mole fractions of the monomeric units for the mobile phase are determined to be 84 ± 5% ethylene and 16 ± 5% propylene. We note that within the limit of the signal-to-noise ratio, the spectra in Figure 5 do not show any signals in the diene region (not shown), suggesting that the mobile polymer in this sample is EPR rather than EPDM. With the above composition of EPR (including potential contributions from amorphous PE; *vide supra*) and the signal intensities of Figure 5b, we determine the PE/EPR copolymer to be a mixture of 35 ± 5% w/w crystalline PE and 65 ± 5% w/w EPR.

In addition to the resonances assigned to PE and EPR, the spectra in Figure 5 exhibit a number of weak but well-defined resonances at 14.7 (o), 23.6 (e), 24.1 (e), 26.2 (e), 73.9 (o), and 169.8 (e) ppm, where the letter in parentheses denotes n-even (e) or n-odd (o) parity for the number of attached protons. Using standard additivity rules for chemical-shift calculations[33] and the information from spectral editing, the last two resonances may be ascribed to a mobile constituent with a methine backbone carbon (73.9 ppm) attached to an ester group exhibiting a carbonyl resonance at 169.8 ppm. We note that these resonances most likely cannot be ascribed to the incorporation of vinyl acetate since for poly(vinyl acetate) the following resonance positions have been determined: $\delta(CH) \approx 68$ and $\delta(CO) \approx 171$ ppm (along with $\delta(CH_3) \approx 22$ and $\delta(CH_2) \approx 41$ ppm).[34]

C. Sample 3 (PS/PE/BR). Figure 6 shows ^{13}C MAS spectra for sample **3** obtained using CP (Figure 6a, $\tau_1 = 800\ \mu s$), single-pulse excitation with relaxation delays of 1 s (Figure 6b) and 160 s (Figure 6c), and MAS SEMUT with $\theta = 0^\circ$ (Figure 6d, positive intensities for all carbons) and $\theta = 180^\circ$ (Figure 6e, up/down intensities for CH_n groups with n-even/n-odd). The heterogeneity of this sample becomes evident by comparison of the CP/MAS with the standard MAS spectra in parts a–c of Figure 6. The CP/MAS spectrum, which favors resonances from the immobile phase, shows a number of broad resonances/shoulders at 40.8, 46.1, 127.0, 128.5, and 146.5 ppm which (along with the spinning sidebands from the aromatic carbons) are ascribed to an immobile phase of polystyrene (PS). Furthermore, the CP/MAS spectrum shows intense resonances at 31.0 and 32.9 ppm from amorphous and crystalline PE, respectively.

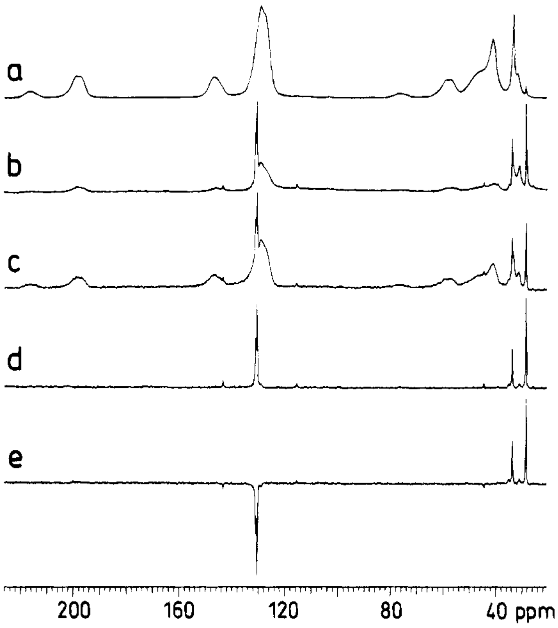


Figure 6. ^{13}C CP/MAS, MAS, and MAS SEMUT spectra ($\nu_r = 5277$ Hz) of sample **3** (PS/PE/BR triblock copolymer): (a) CP/MAS spectrum ($\tau_1 = 800\ \mu s$, 4096 scans, and a relaxation delay of 4 s); (b) MAS spectrum (4096 scans and a relaxation delay of 4 s); (c) MAS spectrum (768 scans and a relaxation delay of 160 s); (d,e) MAS SEMUT spectra recorded using (d) $\theta = 0^\circ$ and (e) $\theta = 180^\circ$.

In addition to the resonances from polystyrene and the amorphous and crystalline phases of PE, the two single-pulse ^{13}C MAS spectra (Figure 5b,c) show narrow resonances from a mobile polymer. As for the copolymer investigated above, these are most conveniently detected and analyzed using MAS SEMUT, which efficiently suppresses resonances from polymer regions having restricted molecular motion. The MAS SEMUT spectra (Figure 6d,e) display four relatively intense resonances which (following the ^{1}H-multiplicity information of the $\theta = 180^\circ$ MAS SEMUT spectrum) have been assigned to *cis*-1,4-butadiene (28.3 and 130.2 ppm) and *trans*-1,4-butadiene (33.5 and 130.7 ppm) monomer units of a butadiene rubber (BR). Using the diad-sequence notation of Katritzky and Weiss,[35] these resonances are more specifically attributed to *cis*- and *trans*-1,4-butadiene units mutually linked in any order (Table 1). The four weaker resonances at 34.9, 44.3, 115.1, and 143.1 ppm can be assigned to the four different carbon atoms of a 1,2-butadiene monomer unit linked to *cis*- and *trans*-1,4-polybutadiene as listed in Table 1. The presence of 1,2-butadiene units in the BR component is further evidenced by the weak resonances at 25.8 and 39.0 ppm originating from *cis*-1,4-butadiene and *trans*-1,4-butadiene, respectively, attached to the 1,2-butadiene. On the basis of the relative signal intensities determined from the ^{13}C MAS spectrum in Figure 6c, the mole fractions of the monomeric units in the BR component are determined to be 59 ± 5% *cis*-1,4-butadiene, 35 ± 5% *trans*-1,4-butadiene, and 6 ± 5% 1,2-butadiene. According to the MAS SEMUT spectrum (Figure 6d), amorphous PE contributes only little to the mobile phase of the PS/PE/BR copolymer. Using the relative intensities from Figure 6c the copolymer is determined to be a mixture of 35% w/w PS, 37% w/w PE, and 28% w/w BR (all ±5%).

Conclusions

Detailed information regarding the structure, dynamics, and composition of complex heterogeneous polymers (copolymers or blends) may be achieved by using appropriate combinations of ^{13}C MAS NMR pulse techniques. In this work ^{13}C NMR signals from mobile (amorphous) and immobile (crystalline) carbons of three unknown (or partially unknown) copolymers have been separated, assigned, and quantified employing a combination of ^{13}C MAS experiments such as single-pulse excitation, cross-polarization methods including CP and CPD, and MAS SEMUT spectral editing. A key experiment in the analysis of heterogeneous polymers is the MAS SEMUT experiment,[8] which selectively detects signals from mobile constituents by complete suppression of signals from carbons in rigid and interfacial environments and furthermore facilitates assignment of the ^{13}C spectra for the mobile phases through spectral editing.

Acknowledgment. The use of the Varian XL-300 spectrometer, sponsored by the Danish Research Councils (SNF and STVF), Carlsbergfondet, and Direktør Ib Henriksens fond, at the University of Aarhus NMR Laboratory is acknowledged. Financial support from the Danish Technical Research Council (STVF, J. no. 16-4722) is also acknowledged. We thank the Aarhus University Research Foundation for equipment grants. We are grateful to several Danish companies for providing the copolymer samples.

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MA9413148