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Motional heterogeneity in acrylate/laurylmethacrylate copolymers probed by two-dimensional solid-state n.m.r.

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Motional heterogeneity in acrylate (AA)/laurylmethacrylate (LMA) copolymers was investigated by the two-dimensional ^{1}H-^{13}C heteronuclear wideline-separation n.m.r. technique. Qualitative information about molecular dynamics is reflected in the width of the proton wideline. It was found that a decrease of the AA/LMA ratio in the copolymer reduces the packing density.

(Keywords: copolymers; nuclear magnetic resonance; molecular dynamics)

A knowledge of the molecular dynamics in copolymers is of great practical interest owing to their widespread technical applications[1]. Solid-state n.m.r. spectroscopy has proved to be a successful method yielding detailed information about molecular dynamics and spatial relations[2]. Spatial relations between various phases can be efficiently probed by spin diffusion measurements[2,3]. Motional heterogeneities can be unravelled with ^{2}H n.m.r. using site-selective substitution of protons by deuterons[4,5]. This usually requires a laborious and expensive synthesis of labelled materials. The site selectivity can also be provided by ^{13}C cross-polarization (CP) and magic-angle spinning (MAS) techniques[6]; however, information about molecular mobility is not present in the spectra. This information is reflected in the width of the ^{1}H line which is broadened by dipolar interactions[7]. These two concepts — structural information from ^{13}C CP/MAS and the information about molecular mobility from ^{1}H spectra — were combined recently by Schmidt-Rohr *et al.*[8] in a two-dimensional (2D) ^{13}C-^{1}H heteronuclear wideline-separation (WISE) experiment. This experiment allows qualitative probing of molecular mobilities in unlabelled materials. The purpose of this communication is to utilize this method to determine motional heterogeneities in variants of a copolymer differing in the molar ratio of the monomeric building blocks. Apparently, in many practical situations qualitative information available from a WISE experiment is sufficient to explain functional properties of materials[9].

Measurements were performed on copolymers of acrylate (AA) and laurylmethacrylate (LMA), with AA/LMA ratios of 12:1, 25:1 and 50:1. All copolymers had a low molecular weight, $M_w \approx 5000$ and $M_w/M_n \sim 2$, as determined by g.p.c. The glass transition temperature T_g in all samples, measured by d.s.c., was above 320 K. D.s.c. curves exhibited a single peak at T_g. A full description of the sample synthesis can be found elsewhere[10]. The n.m.r. spectra were recorded on a Bruker MSL-300 spectrometer equipped with a variable-temperature double-resonance MAS probe. The samples were spun at 3 kHz. The 90° pulse was 4.5 μs. The 2D spectra were taken with up to 80 increments of 8 μs[8,11], and detected after removing spinning sidebands with a total supression of spinning side bands (TOSS) sequence[12]. Experiments were performed at room temperature. All data processing was done using the same line-broadening parameters in order to qualitatively compare the results.

The left-hand side of *Figure 1* shows ^{13}C CP/MAS TOSS n.m.r. spectra of the three copolymers. The spectra exhibit changes in the relative peak intensities at ~32 and ~50 ppm as a function of composition. From this and from the peak assignment in the ^{13}C spectra of homopolymers it is concluded that the resonances in the spectral region between 35 and 10 ppm represent the LMA units. The resonances of the AA units show up between 65 and 35 ppm. The peak around 180 ppm is a superposition of signals from carbons at the carboxyl position present in AA and LMA.

Figure 1 also shows the WISE n.m.r. spectra recorded for the three copolymers. The spectra clearly exhibit spectral resolution along the ^{13}C axis as in the 1D ^{13}C spectra. Along the other axis the ^{1}H dipolar wideline corresponding to the various ^{13}C chemical shift values is given. In the spectrum for composition AA/LMA 12:1, the proton lines of LMA (in front) are narrower than those of AA, indicating motional heterogeneity. From the spectrum of the AA/LMA 25:1 polymer it is also apparent that the LMA proton lines are narrower than those of AA. However, the LMA lines are broader than in the 12:1 composition. Finally, for the AA/LMA 50:1 copolymer the lines of LMA are again somewhat narrower than those of AA. Clearly, WISE spectra correlate the structural information with the mobility in the LMA and AA structural elements. The mobility of the AA and LMA units separately can be inferred from the linewidths in the 2D WISE spectra representing these structural elements. These data are collected in *Table 1*.

Different widths of the proton lines for AA and LMA apparent from *Table 1* indicate motional heterogeneity in the copolymers and an increase of LMA mobility on increasing LMA molar content. The proton lines for AA

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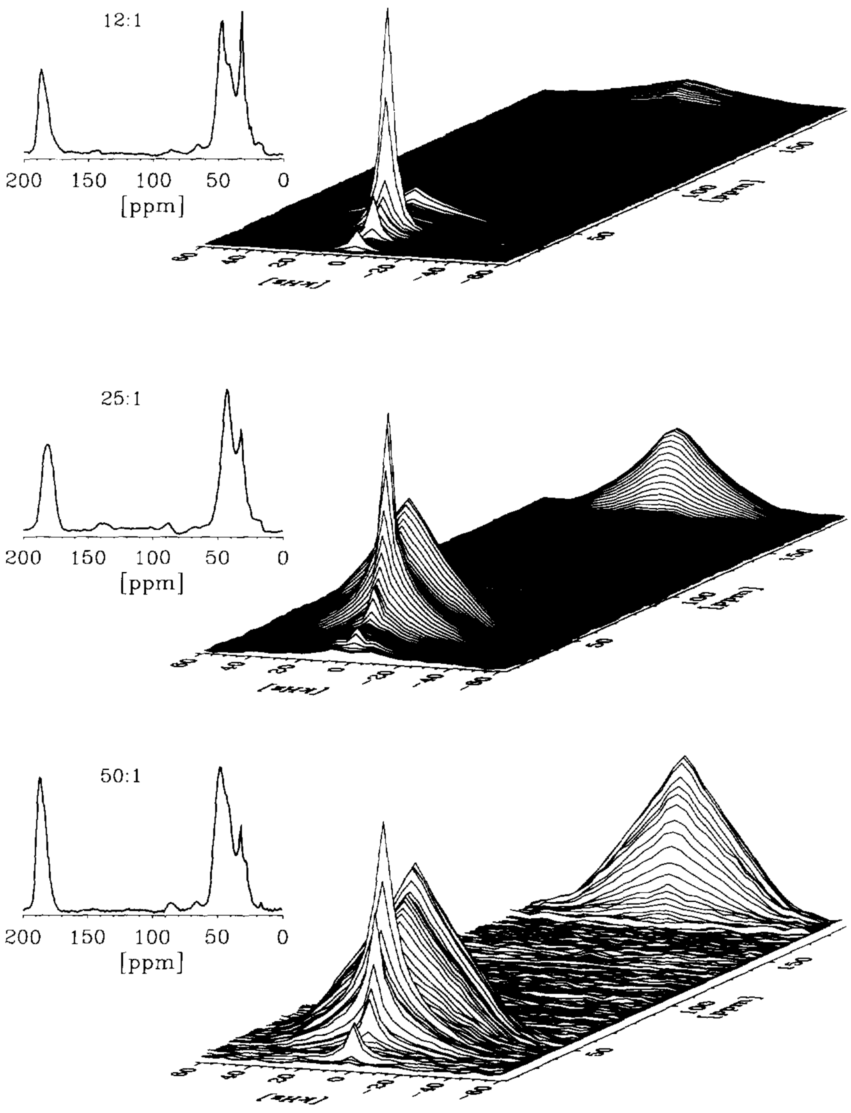

Figure 1 MAS spectra of AA/LMA copolymers with various molar contents of LMA. Left-hand side: 1D ^{13}C CP/MAS TOSS spectra; right-hand side: WISE n.m.r. spectra

at all AA/LMA ratios are wide and structureless. Such widelines are typical for a rigid solid[7].

All n.m.r. experiments were carried out in the glassy state. In the glass the backbone is essentially fixed in the structure[13]. However, the side-group motion, in contrast to the main-chain motion, is not arrested at T_g but remains mobile in the glassy state. This side-chain mobility is reflected in the narrowing of the ^1H line. Observed LMA side-chain mobility in the glass corroborates with the side-chain mobility found in other polymethacrylates[14]. We note that the shape of the ^1H line (*Figure 1*) reflects the nature of the multispin dipolar interaction between protons, and it is virtually impossible to calculate the proton lineshape for a specific motional process. Therefore, the ^1H wideline yields only *qualitative* information, and details of the complex motional mechanism of the side chains found in polymethacrylates cannot be inferred from the spectra[15–17]. In general, molecular motion on the timescale slower than $\tau_c \approx \Delta\omega^{-1} = (2\pi\Delta\nu)^{-1} = 3\,\mu s$, where $\Delta\nu$ is the linewidth at half-maximum, has no effect on proton lines. From the WISE spectra it can be concluded that there is almost no molecular mobility for AA residues on a timescale faster than microseconds, whereas the LMA mobility is roughly on the timescale of 10 μs.

Table 1 Proton linewidths (kHz) for various compositions of the AA/LMA copolymer at half-height and fourth-height of the maximum

	LMA			AA		
Composition	1:12	1:25	1:50	1:12	1:25	1:50
Half-height	3.9	5.6	11.7	29.3	31.3	43.0
Fourth-height	9.8	23.4	27.3	56.6	56.6	64.4

The ^1H widelines obtained for LMA shows the increase of side-chain mobility with increasing molar content of LMA in the copolymer. At the lowest content, AA/LMA 50:1, AA units are densely packed in the glassy environment. The LMA units are scarcely distributed over the chain. This results in a dense packing around the LMA residues, with a low mobility of the relatively large side chains. When increasing the molar content of

LMA by a factor of two (AA/LMA 25:1), the large LMA side chains are more difficult to accommodate in the glassy structure. The packing of the copolymer matrix becomes less dense, giving the LMA side chains more motional freedom. This is reflected in narrower proton lines of LMA units as compared with those in the AA/LMA 50:1 copolymer. Further increase of the molar content of LMA units (AA:LMA 12:1) reduces packing density, increases LMA side-chain mobility and again narrows ^{1}H wideline. These findings are in line with the general observation that the packing in a polymer matrix reduces on increasing the number of carbon atoms in the polymer side groups[18].

This study of AA/LMA copolymers shows that qualitative information about molecular dynamics and packing of copolymers can be easily obtained from WISE n.m.r. experiments. This information is reflected in the width of ^{1}H wideline. It was shown that the increase in molar content of the LMA building blocks, with their large side chain, reduces motional constraints in the polymer matrix.

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