NMR as a Probe of Nanostructured Domains in Ionic Liquids: Does Domain Segregation Explain Increased Performance of Free Radical Polymerisation?

Supplementary Information

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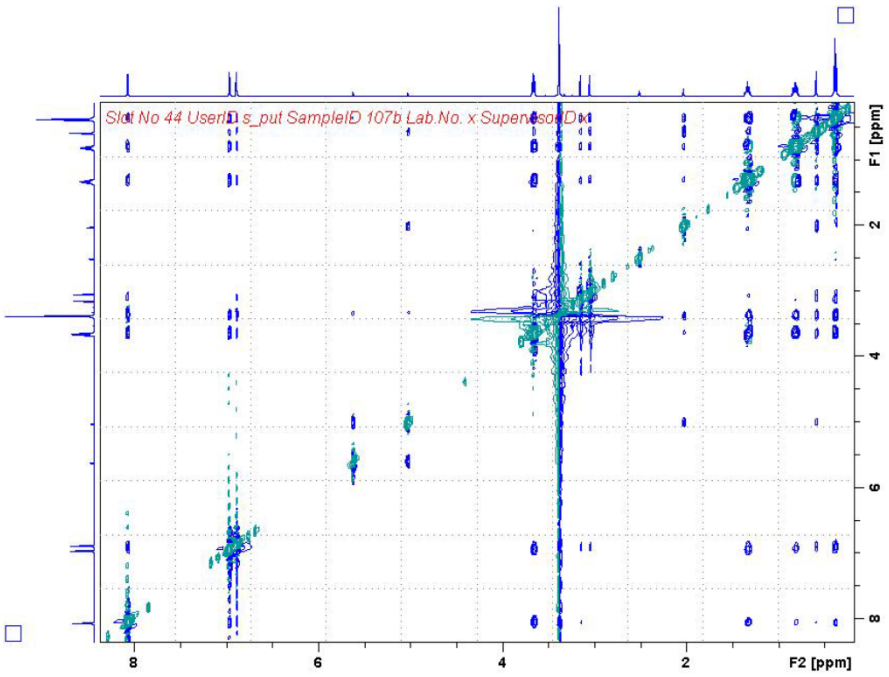
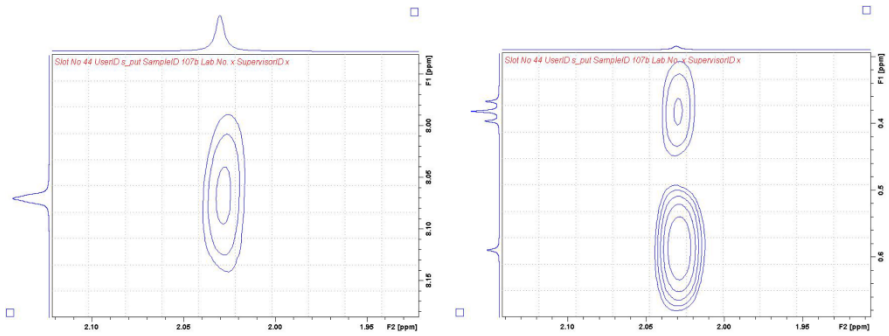
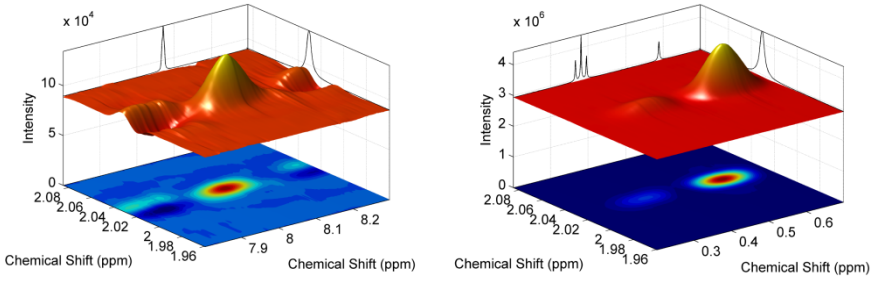
The routine for processing data to obtain the DPIR value was rigidly constrained so as to be as objective as possible. The data processing procedure was as follows:



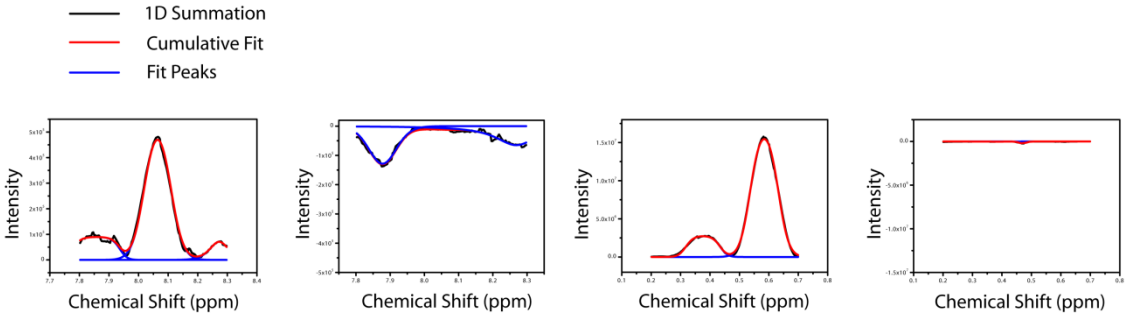
2D ROESY spectra were obtained using a phase alternated spin-lock of 200 ms duration at a field strength of 3 kHz. 256 increments of 2k data points were recorded covering a spectral width of 13 ppm in each dimension with a relaxation delay of 3 s. Data matrices were zero filled and multiplied by a cosine-squared window in both dimensions prior to Fourier transformation.



Small regions containing the cross peaks of interest were strip transformed and baseplane corrected.



The regions of interest were analysed in 3 dimensions to give a clear perspective on artefacts that may interfere with the shape of a 1D summation.



The data were summed in the F2 direction, separating positive (intensity > 0) and negative (intensity < 0) signals, to produce 1 dimensional summations. The 1D summations were then subjected to a peak fitting operation using fixed peak positions, obtained from the relevant ^{1}H NMR spectra. The peak widths at half maximum (FWHM) were fixed and based upon peak widths of the isolated signals of relevant peaks. A Voigt type GL (30 % Lorentzian) peak shape was used for the fittings. The integral of the positive fit peak minus the integral of any negative contributions to the peak area was taken as the integral of the intermolecular ROE.

The DPIR (Table 1) was calculated as the integral of the intermolecular HX-O to H8-C ROE divided by the integral of the HX-O to H2-C intermolecular ROE.

Table 1: Volumetric integral values and DPIR values for all interactions studied.

Volumetric Integral Values of HX-O to H2-C Intermolecular ROE Peaks (Polar Domain)						
	H1-O	H2-O	H3-O	H4-O	H5-O	H6-O
MMA	86950.45211	62029.21458	109853.9526	109853.9526		
MMA2	73823.04521	38639.58488	31622.50811	29467.79727	50986.19471	
MMA3	30750.61414	19203.6598	23284.69666	15618.66925	9061.92356	2652.5581
MMA4	18914.25512	12651.88251	12404.71063	30314.5566	5690.95953	3650.7327
MMA5	10330.99658	7486.69777	28178.27593	72360.61234	798.18785	

Volumetric Integral Values of HX-O to H8-C Intermolecular ROE Peaks (Non-Polar Domian)						
	H1-O	H2-O	H3-O	H4-O	H5-O	H6-O
MMA	148354.0737	159831.9691	567403.7733	567403.7733		
MMA2	122877.1373	112381.0536	160982.0066	155719.8424	314071.1262	
MMA3	73204.56621	69392.24975	132527.4246	95591.74437	74495.37323	50771.81697
MMA4	40289.00604	43874.3261	57601.11325	190790.5953	56025.79318	100738.3041
MMA5	22247.58033	32056.93503	159655.4323	458909.1085	16330.71071	

DPIR Values						
	H1-O	H2-O	H3-O	H4-O	H5-O	H6-O
MMA	1.706190941	2.576720827	5.16507381	5.16507381		
MMA2	1.6644821	2.908443607	5.090741254	5.284407278	6.159924818	
MMA3	2.380588754	3.61349089	5.691610525	6.12035141	8.220702011	19.1406993
MMA4	2.130086846	3.467810112	4.643487056	6.293695724	9.844700684	27.59399617
MMA5	2.153478627	4.281852429	5.665904921	6.341973813	20.45973352	