

Supporting Information

Spherical, particulate poly(ether ketone ketone) by a Friedel Crafts dispersion polymerisation

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Materials

Experimental

Instrumentation

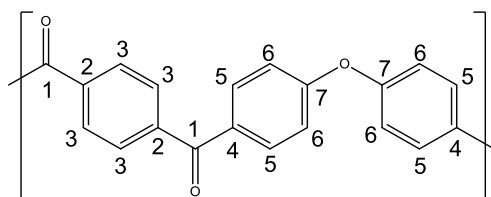
Inherent viscosity (IV) measurements were carried out using Poulten Selfe & Lee glass Ostwald viscometers, size D, in a Townson and Mercer E270 viscometer bath. Measurements were carried out in a solvent of concentrated sulfuric acid at 25 °C. Melt viscosities were recorded on a Malvern Instruments Rosand RH7 capillary rheometer at 400 °C and at a shear rate of 30 s⁻¹, unless otherwise stated. A barrel with length 290 mm and bore diameter 15 mm was used. A tungsten carbide die with length 16 mm and a bore diameter of 1 mm was used, with a 90 ° die entrance. Differential scanning calorimetry (DSC) data were recorded on a Netzsch DSC 200 F3 *Maia*® instrument. Data was recorded using pierced lid aluminium crucibles in a nitrogen atmosphere. Cooling was achieved via a forced air system above 20 °C, or by liquid nitrogen cooling for lower temperatures and fast cooling rates. Data was analysed using *Proteus*® software. Melting point and mol% purity were calculated using the standard protocol in *Proteus*® software. Particle size analysis was recorded on a Malvern Instruments Mastersizer 2000 instrument, coupled with a Hydro 2000MU large volume manual wet dispersion accessory. Analysis was carried out in a dispersant of 50:50 vol% IPA:water, unless otherwise stated. The parameters used were particle refractive index 1.5, particle absorption index 0.1 and dispersant refractive index 1.33. Low resolution mass spectra were recorded on a Fisons Platform spectrometer using electrospray ionisation (ESI) or a Fisons AutoSpec-oaToF spectrometer using electron impact ionisation (EI) or field ionisation (FI). The *m/z* values of major peaks are reported in Daltons. High resolution mass spectra (HRMS) were recorded on a Bruker microToF spectrometer (ESI). ¹H NMR spectra were recorded on Bruker AVN400 (400 MHz), and DRX500 (500 MHz) spectrometers. Chemical shifts (δ_H) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. The abbreviations used to describe multiplicities are as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet) and br (broad). In most cases, first order multiplicities are reported only. Coupling constants (*J*) are given in Hertz (Hz). Two dimensional COSY (correlation spectroscopy) were obtained on a Bruker AVN400 or DRX500 spectrometer. ¹³C NMR spectra were recorded on a Bruker AVN400 spectrometer at 100.6 MHz or a Bruker DRX500 spectrometer at 125.8 MHz with proton decoupling. Chemical shifts (δ_C) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. Assignment was aided by the use of DEPT editing and edited HSQC, performed on either AVN400 or DRX500 spectrometers. ²⁷Al NMR spectra were recorded on a Bruker AVN400 spectrometer at 15 kHz. Chemical shifts (δ_{Al}) are reported in parts per million (ppm). ²⁷Al DPMAS and ¹³C CPMAS solid state NMR spectra were obtained at 104.2 and 100.5 MHz respectively (9.4 T) on a Bruker Avance IIIHD spectrometer, using 4mm O.D. zirconia rotors and MAS rate of 15 and 10 kHz. For ²⁷Al in order to obtain quantitative MAS spectra, a single pulse excitation was applied using a short pulse length (0.23 μ s). 2400 scans were acquired with a 0.1 s delay and a MAS rate of 15 kHz. The ²⁷Al chemical shift was referenced to an aqueous solution of Al(NO₃)₃ (0 ppm). ¹³C CPMAS NMR spectra were acquired using cross-polarization sequence with a variable X-amplitude spin-lock pulse and spinal64 proton decoupling at MAS rates of 8 and 10 kHz. 1500 transients were acquired using a contact time of 2.5 ms, an acquisition time of 25 ms (2048 data points zero filled to 16 K) and a recycle delay of 120 s. All ¹³C spectra were referenced to adamantane (the upfield methine resonance was taken to be at δ = 29.5 ppm on a scale where δ (TMS) = 0) as a secondary reference. Scanning electron microscopy (SEM) was carried out using a Hitachi HT3000 Tabletop SEM. Samples were sputter coated with platinum prior to analysis. Elemental analysis was achieved using built-in energy dispersive x-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was carried out using a VG – Escalab X-Ray Photoelectron Spectrometer VGX900 using Aluminium K α radiation with an energy of 1486 eV. The operating pressure was <1 \times 10⁻⁸ mbar. Samples were attached to the sample stub using double sided tape. The Pass Energy was set at 50 eV for the wide scan of the sample, and 20 eV for the more intense scans of specific areas. The resulting spectra were then analysed using CasaXPS peak fitting software, and sample charging corrected using C 1s as a reference setting at 285.0 eV. Optical microscopy was carried out using a Reichert Polyvar Met Microscope which operates with bright field, dark field and polarisation modules. Images were analysed with digital integration.

Materials

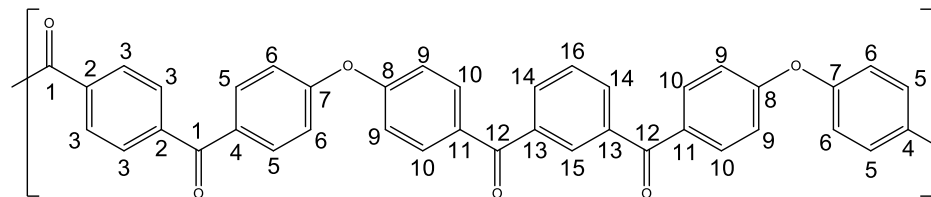
Reagents and solvents

1,4-Bis(4-phenoxybenzoyl)benzene (polymerisation grade) (EKKE) may be obtained by the literature procedure.^{1,2} Terephthaloyl chloride (99+ %) (TPC), isophthaloyl chloride (98 %) (IPC), benzoic acid (99 %, extra pure), aluminium chloride (99 %, extra pure, anhydrous) and benzoyl chloride (98+ %) were obtained from Acros Organics. Dichloromethane (DCM) (99.5 %) was obtained from APC Pure. All reagents and solvents were used as received.

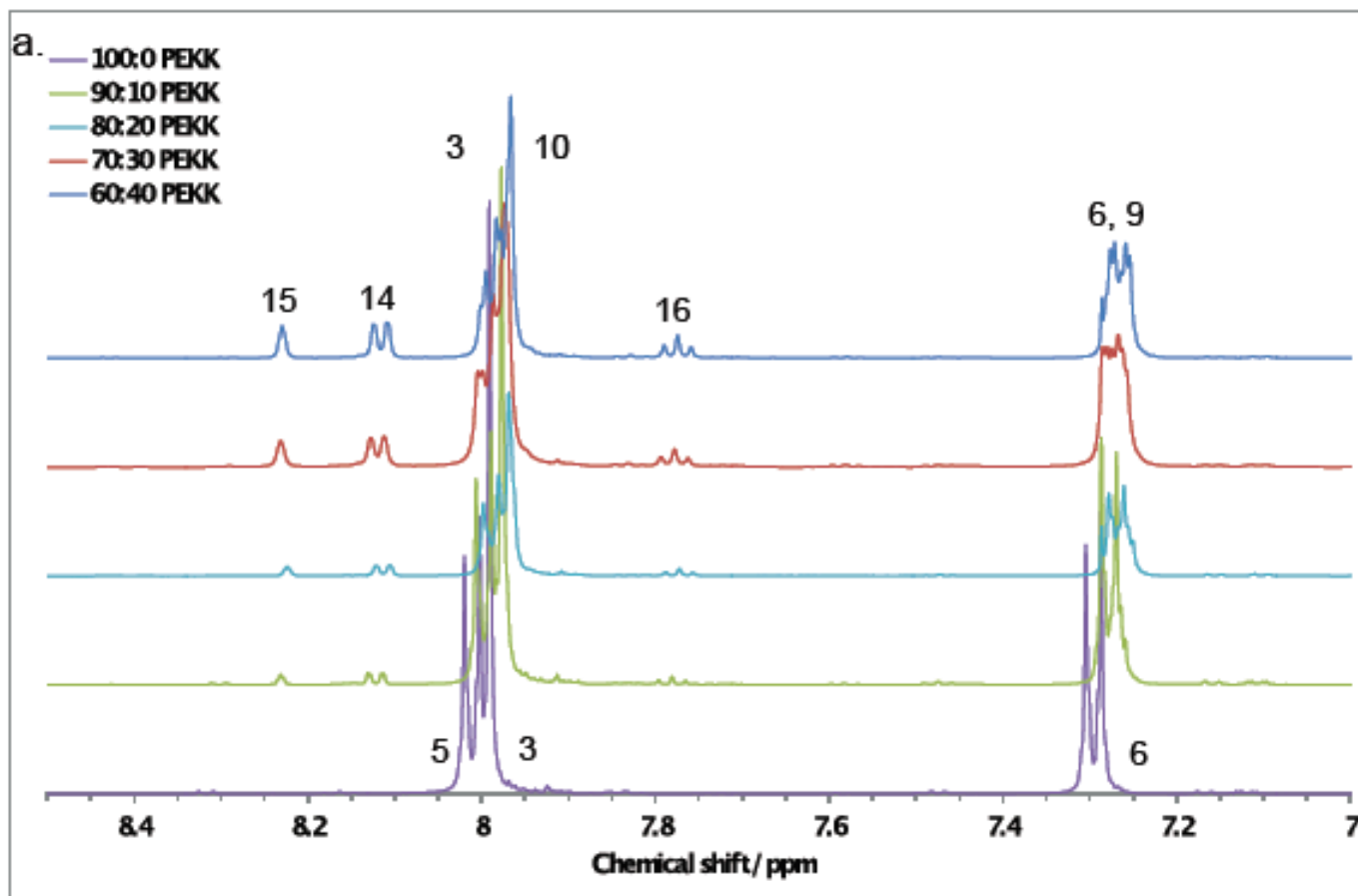
1. D.R. Corbin, E. Kumpinsky, US4918237 1990
2. T. M. Ford, E. Greenville, E. Kumpinsky; A. Vidal, US Pat., US4918237 1990.



100:0 PEKK



90:10, 80:20, 70:30 and 60:40 PEKK



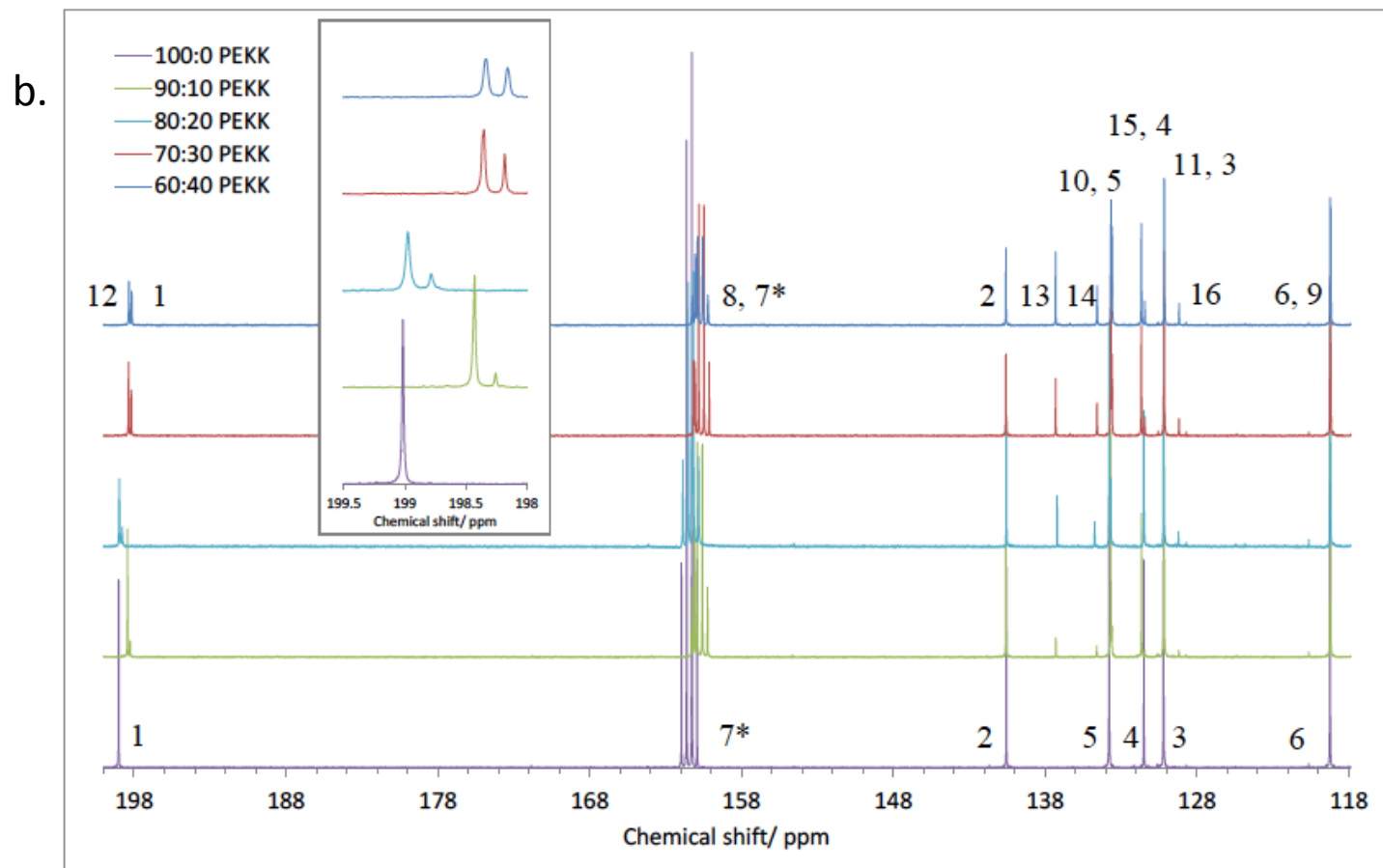


Figure 1. Stacked a. ^1H and b. ^{13}C NMR spectra for the 100:0, 90:10, 80:20, 70:30 and 60:40 PEKK structures, demonstrating the growing in of the peaks associated with the IPC on increasing the quantity of IPC in the monomer feed and polymer. Expansion of δ 198-199.5 ppm, demonstrating the growing in of the isophthaloyl carbonyl peak on increasing the isophthaloyl content of the PEKK

Atom	δ_H		δ_C	
	100:0	60:40	100:0	60:40
1	-	-	161.26**	161.01
2	-	-	119.22	119.21
3	7.98 (m)	7.98 (m)	133.77	133.65
4	-	-	131.48	131.65
5	7.98 (m)	-	199.02	198.33
6	7.27 (d)	7.27 (m)	140.54	140.56
7	-	-	130.19	130.14*
8	-	-	-	164.04
9	-	7.27 (m)	-	119.17
10	-	7.98 (m)	-	133.58
11	-	-	-	130.14*
12	-	-	-	198.16
13	-	-	-	137.30
14	-	8.12 (d)	-	131.42
15	-	8.23 (s)	-	134.56
16	-	7.77 (t)	-	129.16

*Peaks are overlaid

**Peak is overlaid with TFA

Table 1. ^1H and ^{13}C NMR chemical shift data for the 100:0 and 60:40 PEKK structures, with atoms assigned as detailed in Figure 1, and splitting patterns for ^1H NMR spectra

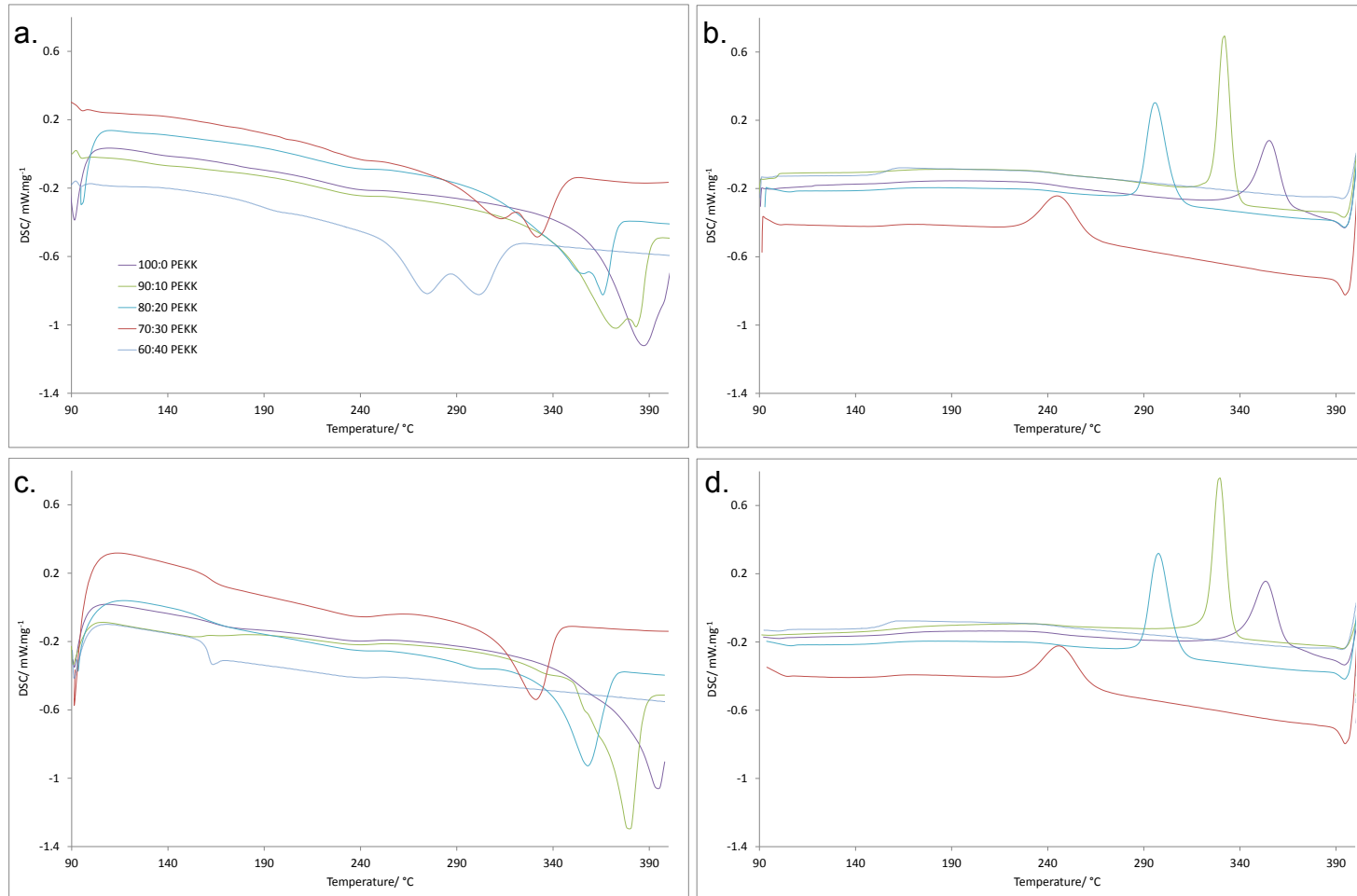


Figure 2. DSC traces for two continuous heating ($20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) and cooling cycles ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) of 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs, a. The first heating cycle of the particulate polymer from $90\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$, b. The first cooling cycle of the sample from $400\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$, c. The second heating cycle of the now consolidated sample from $90\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$, d. The second cooling cycle of the sample from $400\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$

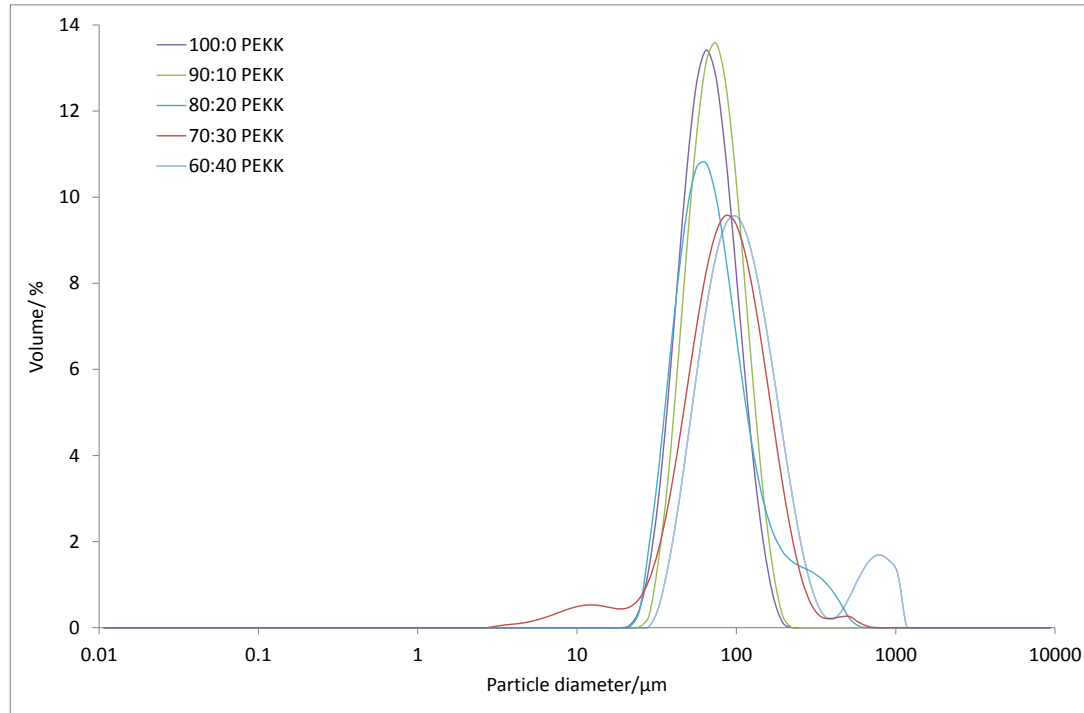


Figure 3. Particle sizing distributions for 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs, as recorded by Mastersizer light scattering in 50:50 IPA:water solvent.

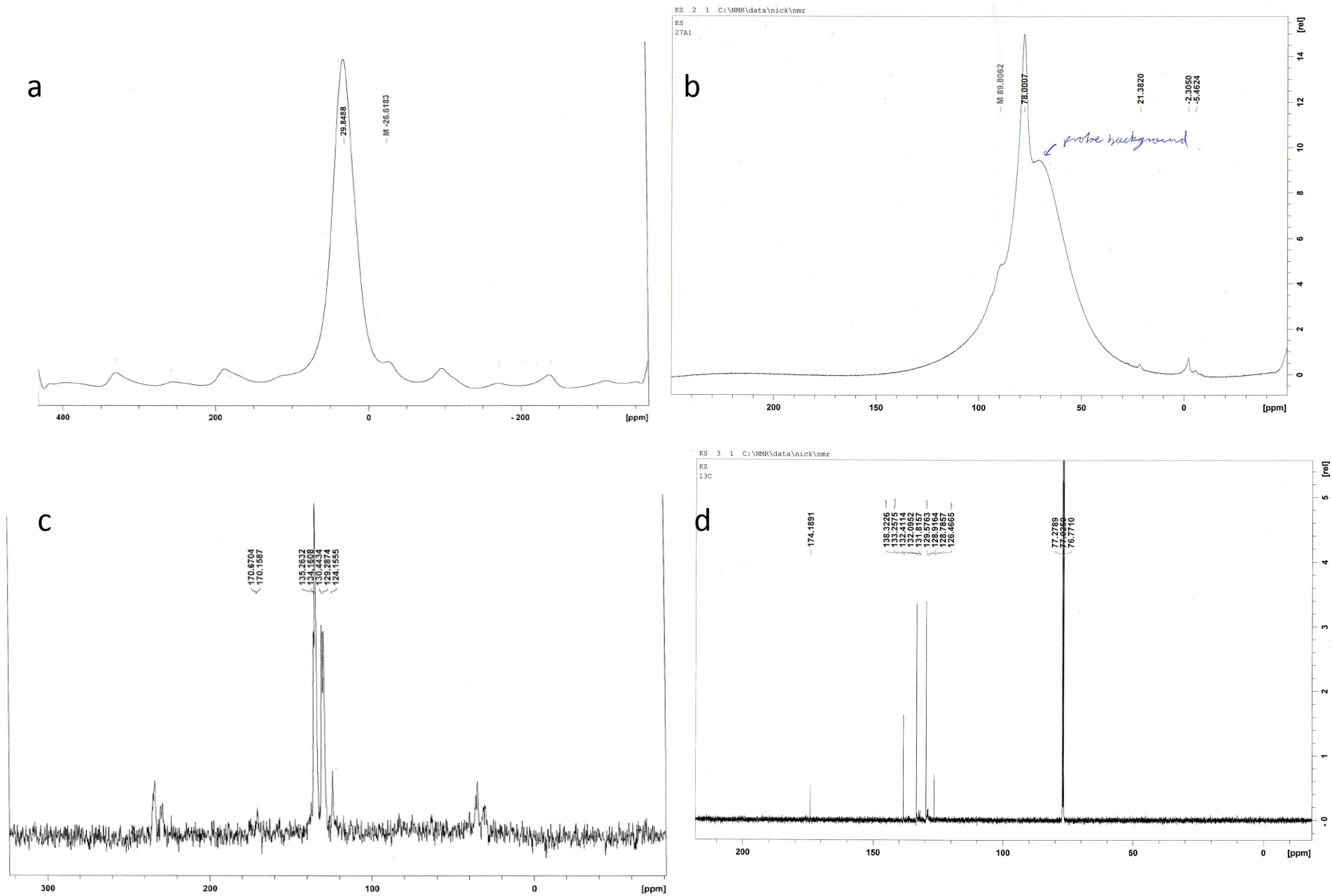


Figure 4. Spectra for the isolated dispersant (a) solid state ^{27}Al NMR; (b) solution ^{27}Al NMR; (c) solid state ^{13}C NMR; (d) solution ^{13}C NMR.