Electronic Supplementary Information

Experimental

Acrylic acid, methacrylic acid, ethanol and methanol were obtained from Sigma-Aldrich and used as received.

Low temperature crystal growth

Methacrylic acid

Methacrylic acid was drawn into a glass capillary (*o.d.* 0.3 mm) and the ends flame-sealed in order to isolate the sample. The sample was placed on a Bruker-Nonius APEX II diffractometer equipped with an Oxford Cryosystems low temperature device operating at 273 K.[1] At this temperature the liquid crystallised as a coarse powder. The temperature of the cryostream was increased towards the melting point (287 K) until a front was observed between the crystalline phase and the liquid. The cryostream was slowly cooled to 273K in order to grow a single crystal; this was verified by obtaining a matrix. The crystal was cooled to 123 K for data collection with no deterioration of the sample indicating that the phase grown at 273 K was stable to 123 K (the unit cell parameters were determined at 273 K, 203K and 123K).

High-pressure crystal growth

A Merrill-Bassett diamond anvil cell[2] was equipped with 600μm culet diamonds attached to tungsten carbide backing discs. A 300um hole was drilled in a preindented 250 um thick tunsten foil to serve as the sample chamber. A piece of ruby was placed in the chamber so that the pressure could be measured *in-situ* using the Ruby fluorescence technique.[3]

A novel loading technique was used in these experiments in order to study these two compounds. A 50:50 by volume solution of acrylic acid in 4:1 methanol:ethanol was prepared and mixed thoroughly. The 4:1 methanol:ethanol mixture is present as the pressure-transmitting medium (PTM). This solution was added to the sample chamber of the DAC before enclosing the liquid. Pressure was applied to the sample until crystallisation was induced. This procedure was modified from the gas loading techniques used in the exploration of gases. An example of this technique is the crystallisation of oxygen.[4] The authors loaded a mixture of oxygen and helium into a DAC. On application of pressure the oxygen was crystallised into a hydrostatic He environment.

Due to the potential of polymerisation on heating only a modest heat (~353K) was applied to the cell so that the crystalline powder was annealed into a single crystal. The same procedure was applied to the 50:50 methacrylic acid:PTM solution.

Single crystal X-ray diffraction

The X-ray intensities of all the samples were measured on a Bruker-Nonius APEX II diffractometer using Mo-Kα radiation. The data collection and processing procedures for the high-pressure samples was carried out using the those outlined in Dawson *et al.*[5] Integration of each crystal was performed using SAINT[6] implementing the dynamic masking procedure described in Dawson *et al.*[5] The absorption correction was applied using programs SHADE[7] and SADABS.[8] The intensities for the low-temperature phase of methacrylic acid were collected at 123 K and the integration of these was performed using SAINT. An absorption correction was applied using SADABS.

All phases were solved by direct methods (SIR-92) and refined against F^2 using all data. Despite the low data completeness of the high-pressure phases, all non-H atoms were refined anisotropically with the alkyl hydrogens placed and allowed to ride on their parent atoms. The carboxyl hydrogen in each sample was found on the difference map and restrained to the oxygen atom (0.85 Å) before allowing it to ride on the parent atom. The crystal structure data for all datasets are found in Table ES1.

All crystal structures were visualised using the programs Mercury.[9] Other structural analyses were carried out using PLATON[10] incorporated in the crystallographic suite WIN-GX.[11] The numbering scheme for acrylic acid is consistent with the numbering scheme found in Boese *et al.*[12]

Raman measurements

Raman and pressure measurements were conducted on a ThermoScientific DXR Raman miroscope using a 532 nm laser. The spectra were analysed using OMNIC software.[13]
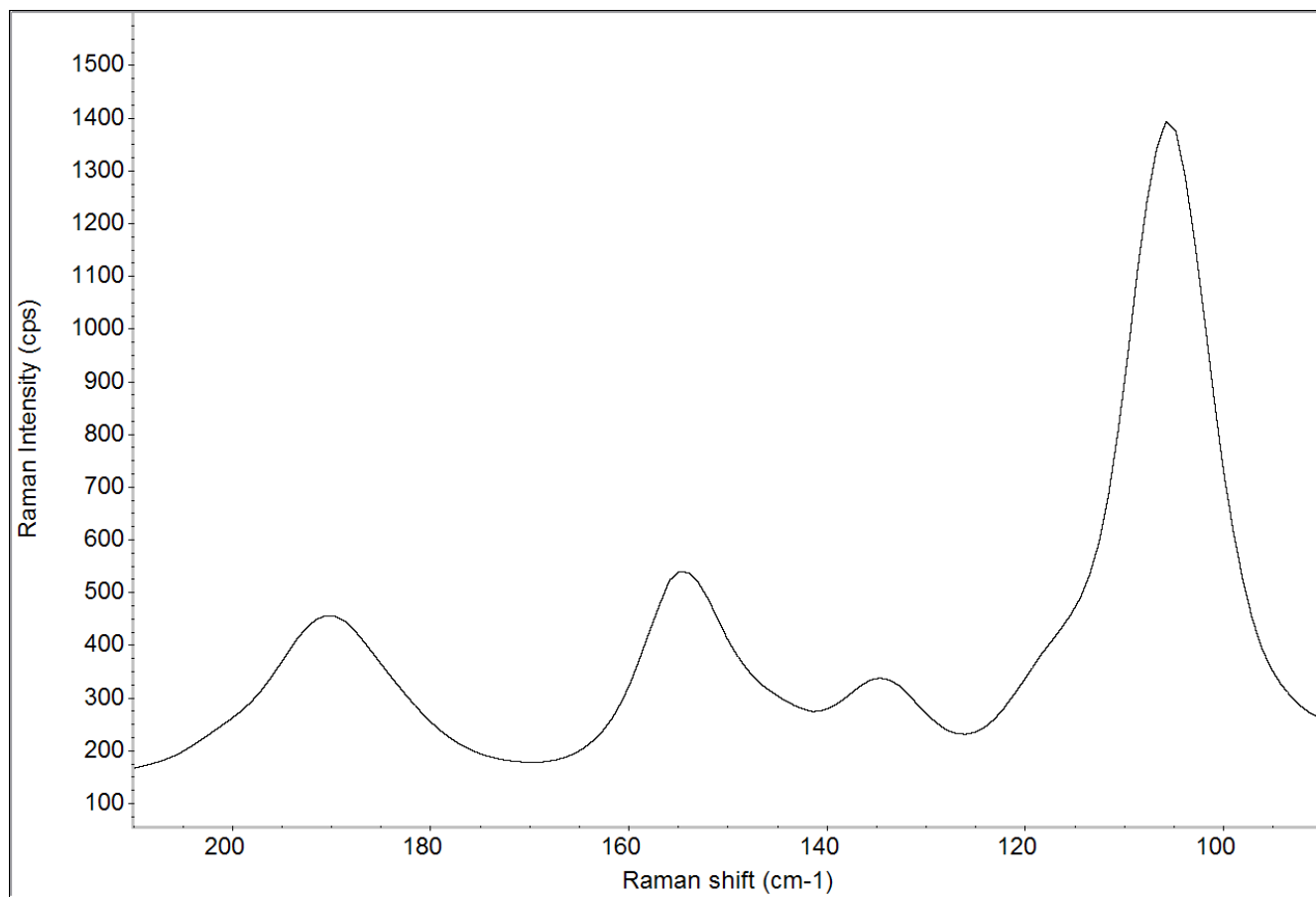
Figure ES1: The Raman spectra (100-200 cm^{-1}) of Phase II of acrylic acid. This spectrum was very similar to that observed by Murli and Song when they compressed acrylic acid directly to 3.3 GPa (see Figure 5a of reference 4 in main text).

Polymer of methacrylic acid from Phase II

a)

Polymer of methacrylic acid from Phase I

3000 2000 1000
Raman shift (cm-1)

Polymer of Acrylic acid from Phase II

b)

Polymer of Acrylic acid from Phase I

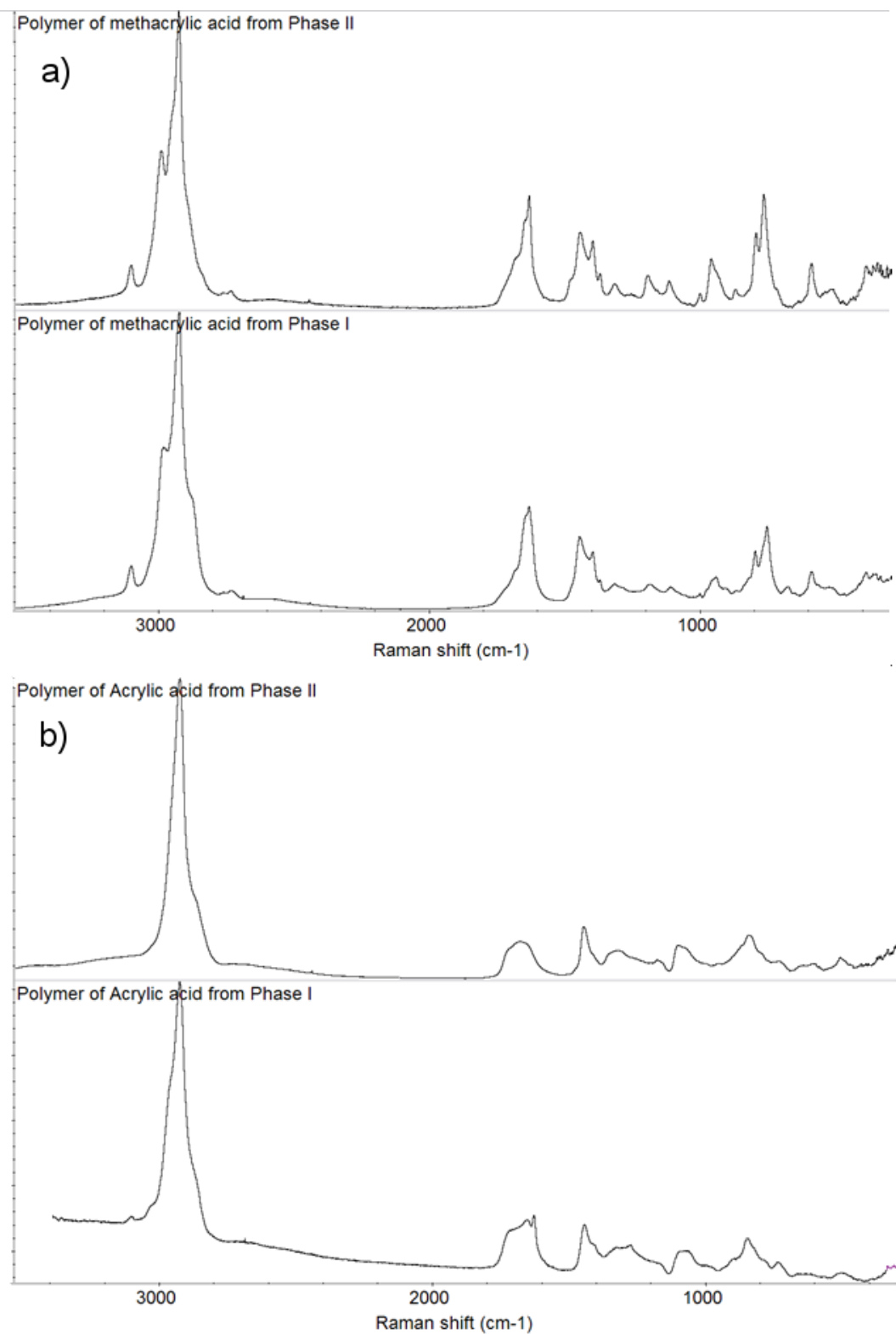3000 2000 1000
Raman shift (cm-1)

Figure ES2: The Raman spectra of a) methacrylic acid and b) acrylic acid from Phases I and II.

Table ES1. Experimental details

	(1)	(2)	(3)	(4)	(5)
Chemical formula	$C_3H_4O_2$	$C_3H_4O_2$	$C_4H_6O_2$	$C_4H_6O_2$	$C_4H_6O_2$
M_r	72.06	72.06	86.09	86.09	86.09
Crystal system, space group	Orthorhombic, *Ibam*	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Pressure (GPa)	0.4	0.65	0.0001	0.3	1.5
Temperature (K)	293	293	123	293	293
a, b, c (Å)	9.959 (3), 11.667 (3), 6.3044 (11)	5.1352 (10), 9.802 (3), 6.850 (4)	3.8056 (3), 10.4842 (8), 11.6286 (10)	3.8808 (11), 10.616 (6), 11.718 (4)	3.7643 (13), 13.501 (6), 8.308 (5)
β (°)	90	97.28 (3)	91.468 (4)	91.24 (2)	101.22 (3)
V (Å^3)	732.5 (3)	342.0 (2)	463.81 (6)	482.6 (3)	414.1 (3)
Z	8	4	4	4	4
D_x (Mg m^{-3})	1.307	1.399	1.233	1.185	1.381
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.12	0.10	0.10	0.11
Crystal size (mm)	$0.30 \times 0.30 \times 0.05$	$0.30 \times 0.30 \times 0.05$	$0.40 \times 0.10 \times 0.10$	$0.30 \times 0.30 \times 0.10$	$0.30 \times 0.10 \times 0.05$
T_{min}, T_{max}	0.82, 0.99	0.78, 0.99	0.93, 0.99	0.76, 0.99	0.77, 0.99
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	1615, 201, 113	947, 267, 189	3210, 920, 748	1966, 350, 197	602, 297, 198
R_{int}	0.034	0.052	0.013	0.034	0.053
θ_{max} (°)	23.3	23.3	26.5	23.3	23.2
$R[F^2 > 2\sigma(F^2)], R(F^2), S$	0.043, 0.119, 1.03	0.041, 0.089, 1.05	0.032, 0.087, 0.98	0.059, 0.135, 1.08	0.046, 0.112, 1.07
No. of reflections	201	267	920	350	297
No. of parameters	34	46	55	55	55
No. of restraints	31	0	0	28	0
ρ_{max}, ρ_{min} (e Å^{-3})	0.21, -0.28	0.31, -0.29	0.17, -0.17	0.27, -0.23	0.32, -0.34

Table ES2. Intermolecular Interactions (Distances have been normalised: O-H 0.98 Å; C-H 1.08 Å)

Compound	Donor	Acceptor	O...O (Å)	O-H (Å)	H...O (Å)	D-H...O (°)
Polymorph I						
Acrylic acid at 125 K[a]	O1-H1	O2[i]	2.6529(9)	0.79(3)	1.86(3)	176
	C2-H2	O2[ii]	3.336	1.08	2.32	155
	C3-H3	O1[iii]	3.538	1.08	2.59	147
Acrylic acid 0.4 GPa	O1-H1	O2[i]	2.6507(8)	0.98	1.68	170
	C2-H2	O2[ii]	3.3301(10)	1.08	2.39	156
	C3-H3	O1[iii]	3.5218(11)	1.08	2.57	147
Methacrylic acid at 123K	O1-H1	O2[iv]	2.622(1)	0.98	1.64	178
Methacrylic acid at 0.3 GPa	O1-H1	O2[iv]	2.631(8)	0.98	1.65	178
Polymorph II						
Acrylic acid 0.65 GPa	O1-H1	O2[v]	2.648(4)	0.98	1.67	175
	C2-H2	O2[vi]	3.293(4)	1.08	2.31	150
	C3-H3	O1[vii]	3.438(5)	1.08	2.45	152
Methacrylic acid at 1.5 GPa	O1-H1	O2[viii]	2.621(5)	0.98	1.65	167
	C4-H5	O2[ix]	3.476(6)	1.08	2.43	161

[a] From ref 6 in main paper.

Symmetry Operators: i -x, -y, z; ii ½+x, ½-y, -z; iii ½-x, ½+y, -z; iv –x, 1-y, 1-z; v 1-x,1-y,-z; vi 2-x, -1/2+y, ½-z; vii 1+x, ½-y, ½+z; viii 2-x, -y, 1-z; ix -1+x, ½-y, -1/2+z

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[13] Thermo Fisher Scientific Inc., Omnic for Dispersive Raman 8.1.106, Copyright © 1992-2009.