Electronic Supplementary Material (ESI) for Polymer Chemistry.


Supporting Information

# A Self-Crosslinking monomer; α-Pinene Methacrylate. Understanding and Exploiting Hydrogen Abstraction

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| **Hydrogen abstraction** | **IBMA** | **αPMA** | **βPMA** |
|---|---|---|---|
| **1** | - | **29.6** | **11.4** |
| **2** | 43.8 | **32.7** | **28.7** |
| **3** | 49.6 | 53.0 | 39.7 |
| **4** | 82.4 | 78.6 | 65.2 |
| **5** | 47.3 | 78.2 | 66.3 |
| **6** | 48.0 | 75.1 | 60.1 |
| **7** | 60.6 | * | 40.7 |
| **8** | 59.8 | 75.0 | 53.3 |
| **9** | 59.1 | 68.7 | 59.3 |
| **10** | 64.6 | 81.3 | 71.1 |

**Table S1.** The energies in kJ/mol of each hydrogen abstraction from IBMA, αPMA, and βPMA (see figure DFT.a in the main text for atom labels). The lowest energy abstractions are in bold. *The removal of hydrogen atom 7 in αPMA resulted in a radical on position 1 following optimisation.

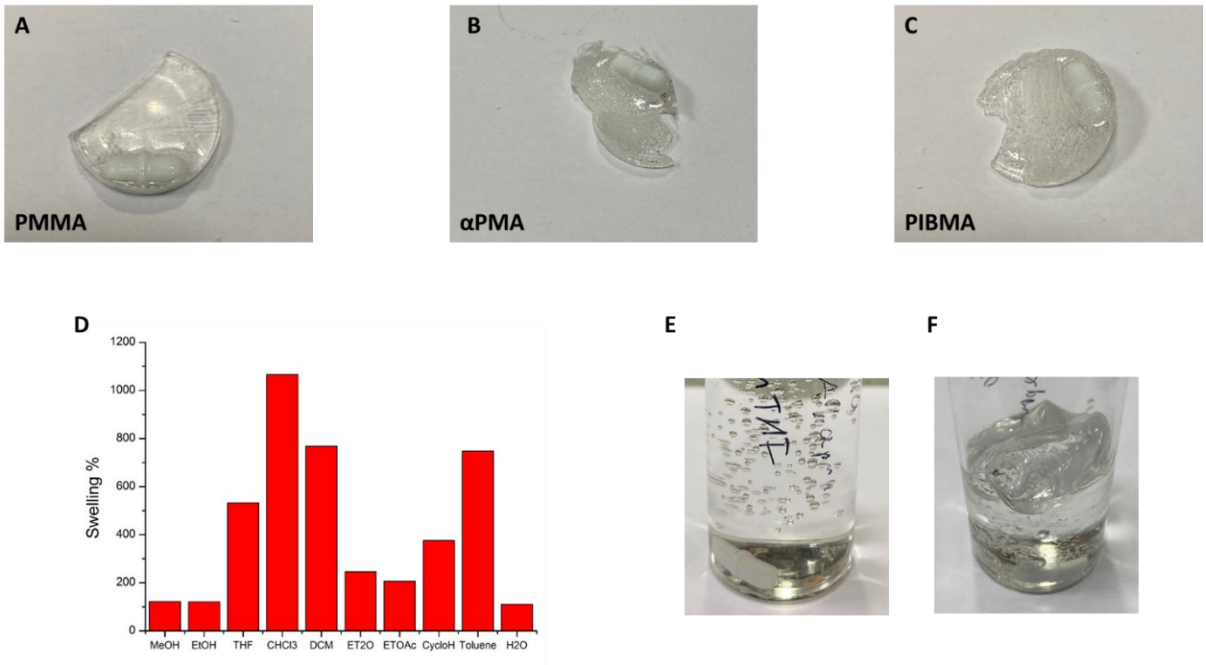


**Figure S1.** A-B-C) Physical appearance of PMMA, PαPMA and PIBMA after 24h reaction; D) PαPMA swelling% in different solvents and E) THF insolubility of PIBAM- PαPMA 70/30% mol/mol (air bubbles are visible and persistent after shaking) and F) tendency to swell of PMMA- PαPMA 70/30% mol/mol.

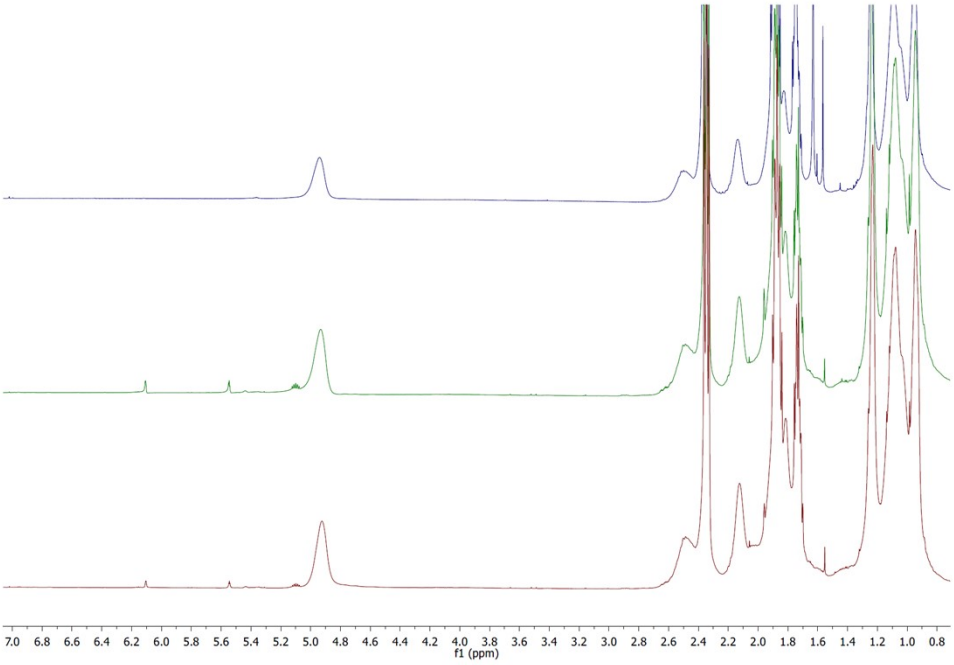


**Figure S2.** αPMA $^{1}$HNMR spectra after 24h reaction at 1:4 (bottom), 1:6 (centre) and 1:1,5 (top) monomer:solvent dilution.

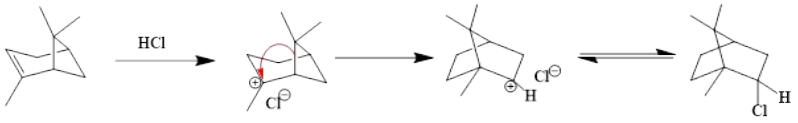


**Figure S3**: Mechanism for the rearrangement of α-pinene through the addition of HCl to form bornyl chloride.

## Electron Paramagnetic Resonance (EPR)

Electron paramagnetic resonance (EPR) is a technique commonly employed to monitor the propagating radicals during radical polymerisations.[1-4]

In situ EPR was utilised to monitor the bulk free radical polymerisation of αPMA, initiated by AIBN, in an attempt to identify both the propagating radicals and the presence of any new radical centre that might be responsible for the crosslinking reaction. Although it was promising that the propagation of αPMA exhibited the same 9-line spectrum as MMA (Figure S4(b)), we were not able to see the next step, i.e., to ascertain the position of the radical formed upon the pendant group which leads to crosslinking. This is most likely due to the proposed radical on the pendant group having a short lifetime, and also being present in only a very low concentration in comparison to the propagating

radical, and these are the likely reasons that it could not be detected under the measurement conditions.

Our data showed an initial radical with a 1:3:3:1 hyperfine splitting pattern, indicating that the radical was coupling to three equivalent $I = ½$ nuclei, and therefore adjacent to a $CH_3$ group. The EPR spectrum of the AIBN initiating radical is well established and shows as a quintuplet of triplets, which was not seen in this work.[5] This 1:3:3:1 pattern is therefore attributed to the initial propagating tertiary radical on a short oligomeric chain, situated close to the AIBN end group (Figure S4(a)). We deduce that due to the strong electron withdrawing nature of the cyano moiety, the $CH_2$ group β to the tertiary radical (Figure S4(a), position A) does not contribute to the initial splitting. Therefore, only the $CH_3$ group β to the tertiary radial (Figure S4(a), position B) interacts, and hence leads to the 1:3:3:1 splitting pattern.

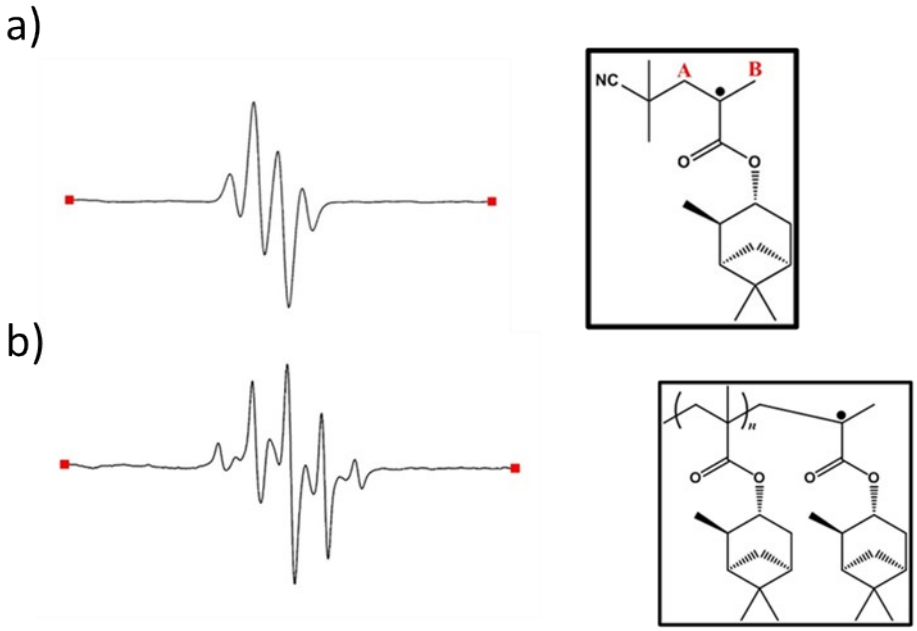


**Figure S4**. (a) Initial (within first 5mins) in situ X band (9.4 GHz) EPR spectrum of the polymerisation of α-pinene methacrylate at 65 °C showing 1:3:3:1 splitting pattern. (b) 9-line in situ EPR spectrum of the propagation of αPMA at 65 °C.

Within the first 5 minutes of the experiment, this splitting pattern changed to a 9-line spectrum that can be attributed to the tertiary propagating radical of αPMA (Figure S4(b)) in which the effect of the no longer adjacent CN group is now lost. As a control experiment, we followed the polymerisation of MMA at 65°C. Here, there was no observable initial 1:3:3:1 splitting pattern, but the more complex 9-line spectrum was present. This is most likely due to a much faster initiation period for MMA, meaning that the contribution by the AIBN end group was simply too fast for our measurements. This corresponds well with what has been observed previously by others for the propagation of MMA.[5-7]It has been proposed that this 9-line spectrum is actually derived from a single radical by the overlap of five and four line spectra; because interaction of the five β protons ($CH_2$ and $CH_3$) with the radical are limited by rotational restrictions, meaning the radical can only interact with either the $CH_3$ or the $CH_2$ protons, leading to the appearance of a 9-line spectrum.[8]

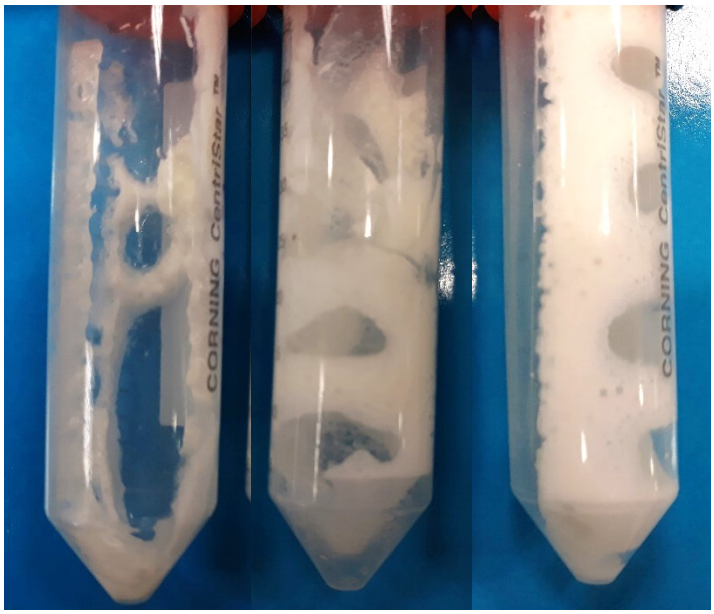


**Figure S5**: Images of PαPMA polyHIPE at 80, 85 and 90 v% water (internal phase) polymerised using 5 wt% SPAN-80 emulsifier.

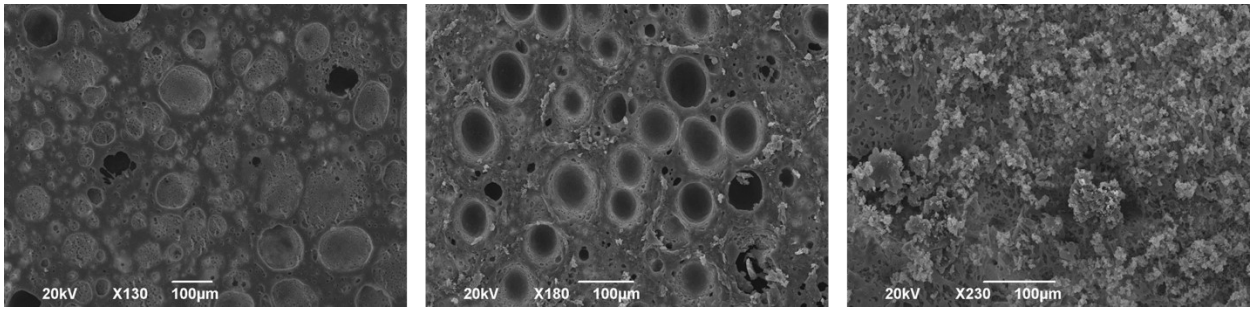


**Figure S6:** SEM images of PαPMA polyHIPE at 80, 85 and 90 v% water (internal phase) polymerised using 20 wt% SPAN-80 emulsifier which did not lead to a stable HIPE.

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