2,2,5,5-Tetramethyloxolane (TMO): An Unusual Ether Which Can Replace Hazardous Hydrocarbon Solvents

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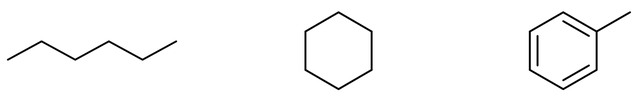
HAZARDOUS HYDROCARBON SOLVENTS

Wide range of applications
- Coating industry
- Reaction media
- Liquid-liquid extractions

Solvent properties
- Non-polar
- Volatile
- Toxic, Petroleum-based

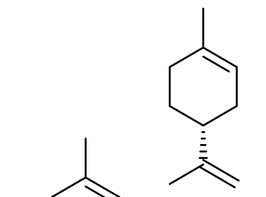


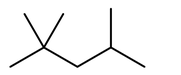
Property	Hexane	Cyclohexane	Toluene
B.p. / °C	68	81	111
δ_D / $MPa^{0.5}$	14.9	16.6	18.0
δ_P / $MPa^{0.5}$	0.0	0.0	1.4
δ_H / $MPa^{0.5}$	0.0	0.0	2.0

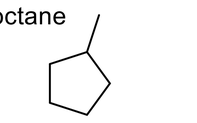
Hexane	-	Suspected of damaging fertility[1]
Cyclohexane	-	Persistent/Bioaccumulative/Toxic[1]
Toluene	-	Suspected of damaging the unborn child[1]

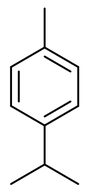
RECENTLY PROPOSED REPLACEMENTS

Bio-based Hydrocarbons

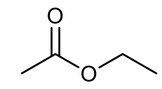


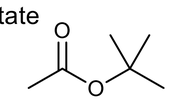


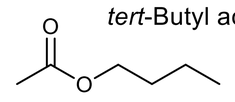




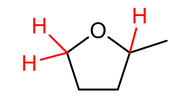
Esters

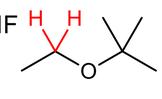


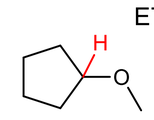




Ethers





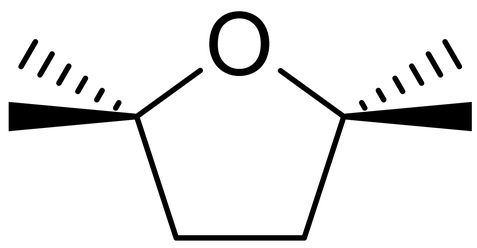


– Non-polar – Bio-based – Lower toxicity	– Easy to remove – Non-polar – Bio-based	– Non-toxic – Easy to remove by evaporation	– Bio-based (except CPME) – Easy to remove by evaporation

– Difficult to remove by evaporation	– Same toxicity as petroleum-based – High mass loss in synthesis – Too volatile	– Difficult to find a balance between low-polarity and ease of removal by evaporation	– Toxicity issues – Forms explosive peroxides

1. ***Easy to synthesise*** *- High atom economy, RME*
2. ***Does not form peroxides‡*** *- Unlike traditional ethers*
3. ***Easy to remove*** *- Low boiling point*
4. ***Low polarity*** *- HSP parameters similar to toluene*
5. ***Predicted low toxicity*** *- Nearest neighbour is eucalyptol*

‡ Even when exposed to UV light and bubbling air in the absence of inhibitors



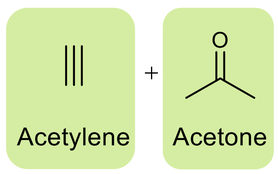
6. ***Performs like traditional hydrocarbon solvents***
7. ***Sustainable feedstocks*** *- Drop-in replacement starting materials can be used*
8. ***Low production cost*** *- Starting (material 2,5-Dimethyl-2,5-hexanediol) already produced commercially[2]*

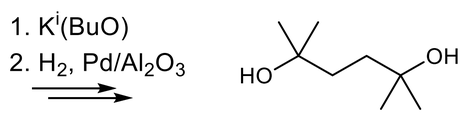
PROPERTIES

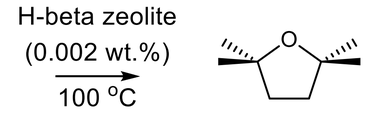
Solvent	Mw / g mol^{-1}	Bp / °C	Mp / °C	ρ / g mL^{-1}	Mol. vol. / cm^3 mol^{-1}	AIT / °C	LEL / v/v%	δD / $MPa^{0.5}$	δP / $MPa^{0.5}$	δH / $MPa^{0.5}$	δ / $MPa^{0.5}$	α	β	π*	Log $P_{(o/w)}$
TMO*	128.21	112	<-90	0.802	151.1	417	0.9**	15.4	2.4	2.1	15.7	0.00	0.77	0.35	1.53
Toluene	92.14	111	-95	0.867	106.6	522	1.1**	18.0	1.4	2.0	18.2	0.00	0.10	0.51	2.73
Hexane	86.18	69	-95	0.661	131.4	225	1.1	14.9	0.0	0.0	14.9	0.00	0.00	0.00	4.00
THF	72.11	66	-108	0.883	81.9	321	2.0	16.8	5.7	8.0	19.5	0.00	0.58	0.59	0.46
2-MeTHF	86.13	78	-136	0.854	100.2	270	1.5	16.9	5.0	4.3	18.1	0.00	0.58	0.53	0.54

*Data first reported in Ref 3; **When molecular weight (Mw) and density (ρ) are taken into account, TMO is found to perform better than toluene with respect to LEL.

SYNTHESIS





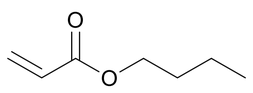


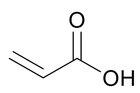
• Conversion of Diol (final step†)	100%
• Selectivity for TMO (final step†)	>99%
• Reaction mass efficiency (total process)	93%
• Atom economy (total process)	96%

† The final step has been patented by Nitto (Ref. 4a)

APPLICATION TESTING

Pressure-sensitive adhesive (PSA) production[3,4b]

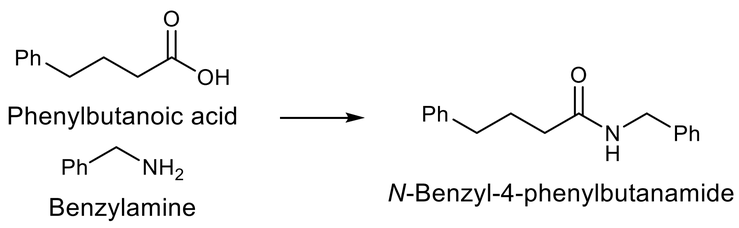


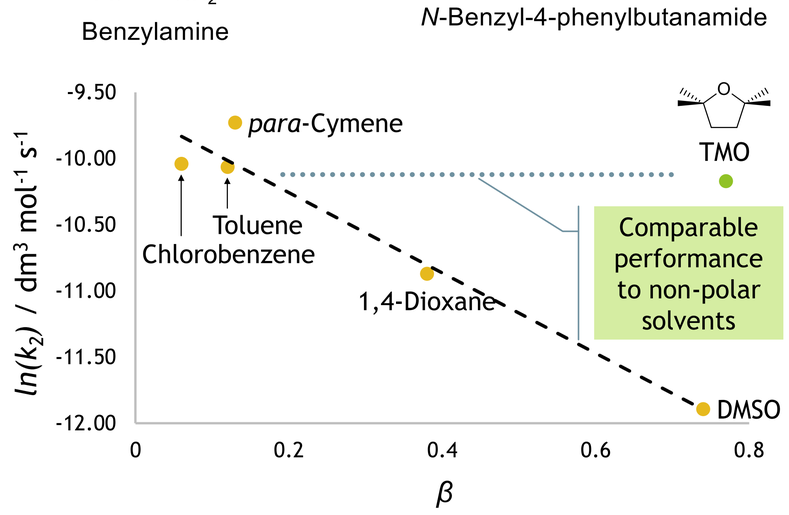


Polymer property	TMO	Toluene	2-MeTHF
Mw / g mol^{-1} (a)	501,000	509,000	9,200
Solid content / wt.% (b)	27.25	31.00	31.00
Adhesion / cN $20mm^{-1}$ (c)	809	757	n/a (f)
Cohesion / days (d)	>10	>10	n/a (f)
Tack (wt. supported) / g (e)	291	264	n/a (f)

(a) Measured by GPC at Nitto Europe; (b) percent of solid polymer dissolved in solvent; (c) measured by the breaking load test at Nitto Europe; (d) measured by the shear adhesion test at Nitto Europe, values shown are the time of failure in days; (e) measured by the rolling ball test at Nitto Europe; (f) Not measurable due to the low Mw obtained.

Catalyst-free amidation reaction[3]





SCALE-UP PRODUCTION

- Large scale production carried out in November 2017 at the Bio-Based Europe Pilot Plant (BBEPP) in Gent
- 40 kg of 2,5-dimethyl-2,5-hexanediol
- 80 g H-beta zeolite
- 98% isolated yield
- >99% selectivity for TMO after simple distillation
- 300 kg scale to be carried out in 2018

Acknowledgements and References

I would like to thank Nitto Belgium for funding the initial work; BBI for funding for the subsequent Resolve project; BBEPP for the scale-up synthesis; Clariant for supplying the H-beta zeolite catalyst.

[1] Information on Chemicals (https://echa.europa.eu/information-on-chemicals)
[2] US Patent 6956141B1, 2005
[3] F. Byrne, B. Forier, G. Bossaert, C. Hoebers, T. J. Farmer, J. H. Clark and A. J. Hunt, *Green Chem.*, 2017, **19**, 3671-3678
[4] (a) NL Patent Application No. P32827NL00/WZO; (b) 2016 and P32826NL00/MKO, 2016. (patents pending)

CONCLUSIONS

A greener replacement for hazardous hydrocarbon solvents has been found. Although TMO is classed as an ether based on its structure, it has been demonstrated to perform more like toluene than traditional ethers such as 2-MeTHF or THF in radically-initiated polymerisation and amidation reactions. Additionally, unlike traditional ethers, TMO does not form peroxides even in the absence of peroxide inhibitors. TMO has been successfully synthesised on a 40 L scale at the BBEPP.