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ARTICLE

Unveiling the role of base catalysts in the thiol-Michael addition reaction in liquid crystal oligomers and elastomers

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Ramazan Umut Dinc, Johan Lub, Xianwen Lou, Augustinus J. J. Kragt, and Albert P. H. J. Schenning*

To commemorate our friend and esteemed colleague Joost L. J. van Dongen

Liquid crystal oligomers (LCO) and liquid crystal elastomers (LCE) are currently receiving much attention as stimuli-responsive polymer materials capable of adapting to environmental changes such as light and temperature, resulting in changes in functional properties including shape and colour. The base-catalysed thiol–Michael addition is widely used to synthesize LCOs and elastomers LCEs, yet the role of the catalyst is often overlooked. This study shows that commonly used amine catalysts form base adducts with the liquid crystal building blocks. In case of triethylamine, this side reaction is avoided, enabling a 95% conversion in the thiol-Michael addition reaction used to synthesize LCOs. Thermomechanical analyses of the corresponding LCEs demonstrate that the materials free from nucleophillic base adducts and with a high thiol-Michael addition reaction conversion exhibit a increased Young's modulus and enhanced stiffness and stress-resistant which is likely attributable to a higher cross link density. Our work provides guidelines for the synthesis of liquid crystal oligomers and elastomers, potentially improving the performance of stimuli-responsive materials and devices.

Introduction

The thiol-Michael addition reaction is a widely used "click-chemistry" type of reaction in the polymer chemistry, employed to synthesize and modify polymer materials[1]. In this reaction a thiol group adds to a Michael acceptor, such as acrylates in the presence of a catalyst. The reaction is widely regarded as highly selective, versatile, and operates under mild reaction conditions while affording good yields. Two mechanisms have been proposed in the literature for the thiol-Michael addition: the base-catalysed and the nucleophile-initiated mechanism. In the base-catalysed mechanism, the catalyst acts as a base and deprotonates the thiol to form a thiolate in the initiation step. The thiolate then adds to the acrylate vinyl group. Subsequently, proton donation of the protonated base takes place, and the catalyst molecule continues the next cycles. In the nucleophile-initiated mechanism, the catalyst acts as a nucleophile and adds itself to the vinyl group of the acrylate for the initiation. A thiol then donates a proton to this negatively charged complex becoming a thiolate, after which the reaction propagates similarly as in the base-catalysed mechanism[2]. However, the nucleophile-initiated pathway results in the loss of the catalyst molecule for the subsequent cycles and gives a conjugation side product. It has been reported in the literature that the choice of the catalyst, type of the vinyl containing group, and the solvent highly influences the addition mechanism[3]. Therefore, due to their base properties, amine catalysts have been widely used to facilitate thiol-Michael additions under mild and clean conditions[4] assuming they only follow the base-catalysed mechanism.

Liquid crystal oligomers (LCO) and liquid crystal elastomers (LCE) are currently receiving much attention as 'smart' polymer materials capable of adapting to environmental changes such as light and temperature, resulting in changes in functional properties including shape and colour [5–13]. The base-catalysed thiol-Michael addition reaction is commonly used to fabricate programmable shape and colour changing polymer materials[14–18]. Typical catalysts include dipropylamine (DPA), α-methyl benzylamine (α-MBA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylamine (TEA). One way of synthesizing main chain LCOs is via thiol-Michael addition of a diacrylate liquid crystal and a dithiol, catalysed by an amine as the base. An optical response is often achieved by incorporating a chiral dopant which induces a chiral nematic phase and structural colour. In case of LCEs, the shape changes are generated upon passing the order-to-disorder phase transition, i.e. the nematic-isotropic phase transition temperature (T_{NI}). This phase transition can be programmed by controlling the crosslink density and the nature of the liquid crystal building blocks within the LCEs. The general procedure begins with the base catalysed thiol-Michael addition of a diacrylate liquid crystal and thiol derivatives as crosslinker. Subsequently, the slightly crosslinked polymer is stretched, and the remaining free-acrylates are photopolymerized by UV light exposure to produce the final LCE material[19,20]. Due to the sequential photopolymerization step, the role of the catalyst has not been

Laboratory of Stimuli-responsive Functional Materials and Devices (SFD), Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
*E-mail: a.p.h.j.schenning@tue.nl

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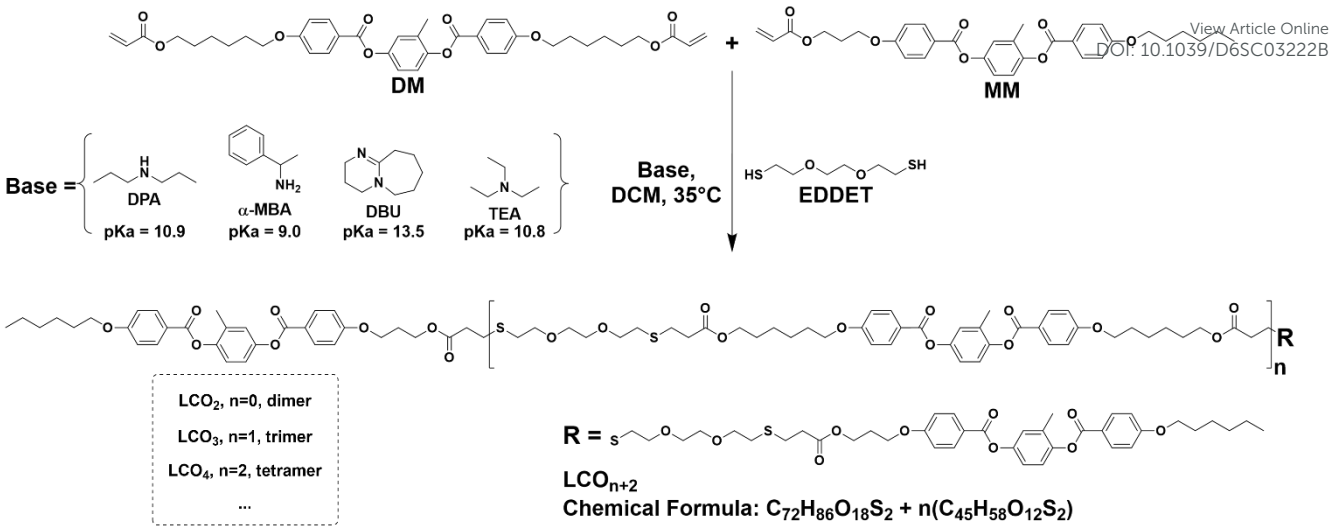

Figure 1 Schematic of the model reaction to prepare LCOs where dichloromethane (DCM) is the solvent.

extensively explored [21–24]. However, potential side reactions during thiol-Michael addition reaction may influence the material's responsive and optical properties, lifetime, and fatigue behaviour.

In this work, we aim to unveil the role of four frequently used amine-based catalysts in the thiol Michael addition reaction in LCOs and LCEs. We evaluated the catalytic performance of these catalysts in a LC oligomerization reaction via thiol-Michael addition. The model reaction involves a diacrylate mesogen (DM), a monoacrylate mesogen (MM) and a dithiol linker (EDDET), resulting end-capped LCOs (**Figure**). For three catalysts, nucleophilic base–acrylate adducts were identified as side products by MALDI-ToF-MS. In contrast, TEA as base did not show nucleophilic addition, and by adjusting the reaction concentration a 95% yield was achieved.

Results and Discussion

We have investigated the role of four commonly used bases, DPA, α-MBA, DBU, and TEA (**Figure**) in the thiol-Michael addition reaction. These bases which contain a tertiary, secondary, or primary amine having high and comparable pKa values, with DBU exhibiting the highest basicity. We aimed to synthesize endcapped LCOs to simplify the analysis. In a typical reaction, 1 eq. of DM , 2 eq. of EDDET and 2 eq. of MM were reacted in the presence of a base in dichloromethane (DCM), at 35°C (**Figure**) in a closed vial under argon atmosphere. The total concentration of the reactants was maintained at approximately 0.23 M, with a catalyst concentration of 14 mM consistent with typical reaction conditions reported for LCO and LCE[14–18]. The reactions were monitored for up to 48 h. Remaining free-acrylates in the mixture were calculated by analysing ^{1}H-NMR spectra[25]. It was observed that DPA, α-MBA and DBU achieved nearly 100% acrylate conversion within 6 h, with no significant increase in conversion upon further reaction up to 48 h. In contrast, the reaction employing TEA as the base reached a plateau of 80 % conversion after 24 h (**Figure a**). Remarkably the conversion decreased to 70 % at 48 h which might indicate an equilibrium reaction. After 48 hours, the reactions were further analysed by GPC. In the GPC profiles (**Figure b**) individual peaks corresponding to oligomers of varying chain lengths are visible and show a range of molecular weight distributions. Oligomers containing one to four mesogenic units are clearly distinguishable[26]. For the ease of

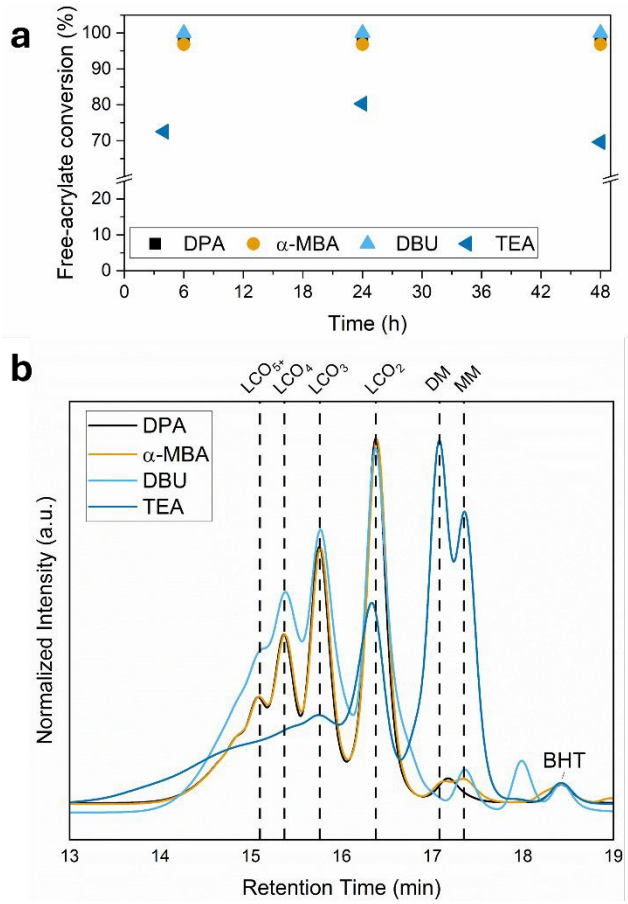

Figure 2 a) Acrylate conversion calculated from the ^{1}H-NMR data as a function of time for the selected catalysts. b) GPC profiles of the molecular distribution of the syntheses after 48th hour and acid-base treatment. "LCO_{2+n}" represents the oligomer size in which monomer units linked with dithiols.

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terminology, LCO_2, LCO_3, LCO_4 are hereafter referred to as dimer, trimer, and tetramer, respectively (Figure 1). The profiles for DPA (**Figure S6**) and α-MBA (**Figure S13**) catalysed reactions appear similar and exhibit comparable polydispersity indexes (PDI) of 1.51 and 1.55 while DBU (**Figure S20**) and TEA (**Figure S27**) showed increased PDIs of 1.81 and 3.52, respectively. In the case of DBU, GPC profile contains an additional distinguished peak at 18.0 min, suggesting the presence of species with a lower molecular weight than MM and DM, which may indicate a cleaving side reaction (vide infra). The least effective catalyst, TEA, shows a relatively higher area percentage of monomers which is consistent with the lower conversion compared to other catalysts. However, it is also noticeable that the TEA catalysed reaction leads to the formation of higher molecular weight species compared than those obtained with the other bases (**Figure b, Figure S27**). Notably, the monomer peaks in the GPC profiles account for more than 3% of the total area in the case of DPA, α-MBA and DBU. These values do not correlate with the remaining free acrylates determined by ^{1}H-NMR (<3%), suggesting the presence of the possible side products that do not contain free acrylate moieties.

To investigate the discrepancy between the ^{1}H-NMR and GPC results, the samples were further analysed using MALDI-ToF-MS (**Figure 3**). In case of the DPA catalysed sample, the analysis revealed no unreacted monomer signals. Instead, the presence of dimers, trimers and tetramers were observed (**Figure b**) consistent with the GPC results. Remarkably, additional low-intensity peaks indicating base reacted LCO species. The presence of DPA adducted dimers, trimers and tetramers suggests a nucleophilic addition of the base (**Figure a**) during the thiol-Michael reaction. Similarly, MALDI-ToF-MS analyses of the α-MBA and DBU catalysed samples revealed the presence of base reacted LCOs, alongside the expected LCO species (**Figure S15, S22**). Additionally, in the DBU catalysed reaction, trace of a cleaved DM product was found, likely arising from a reaction of DBU with the sequential aromatic ester linkage of the mesogenic groups. The presence of this cleavage product supports the low molecular weight peak at 18.0 min in corresponding GPC profile of the same reaction (**Figure b, Figure S21**). Finally, in the TEA catalysed sample, the MALDI-ToF-MS analysis revealed only the expected LCOs with no evidence of nucleophilic addition to the acrylate groups. The absence of TEA adducts may be attributed to steric hinderance associated with the tertiary amine structure of TEA. Interestingly, traces of intermediate molecules with thiol-end groups were detected together with signals corresponding to free DM and MM (**Figure S29**) which is consistent again with the lower conversion compared to other catalysts. The molecular structures and summary table of the calculated and found molecular weights obtained from MALDI-ToF-MS analyses are

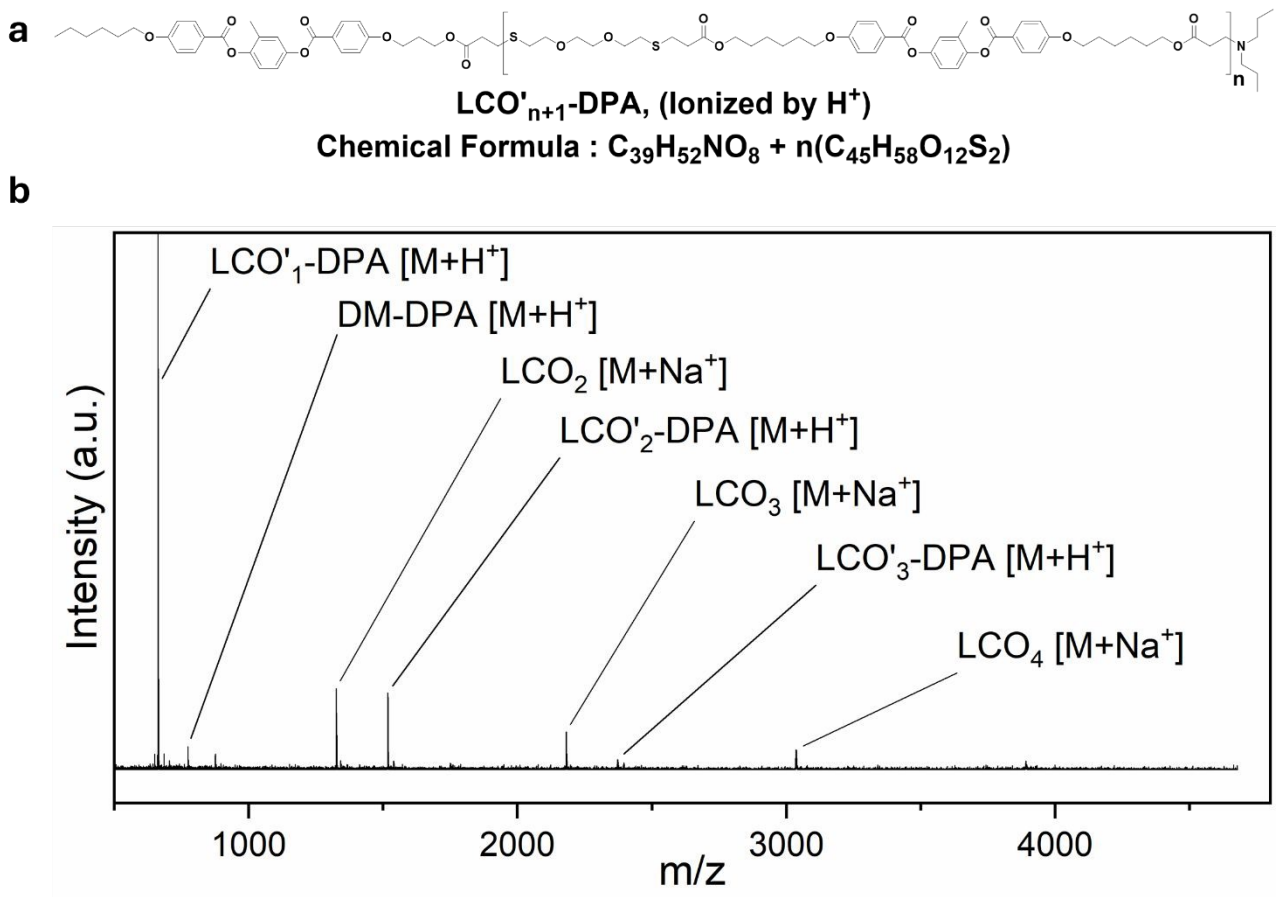

Figure 3 a) The molecular structure of DPA reacted base adduct. b) The MALDI-ToF-MS analysis of the DPA catalysed thiol-Michael addition, showing DPA reacted base adducts alongside typical LCOs m/z values.

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provided in **Figure S30** and **Table S1**. Among these bases, only TEA showed no evidence of nucleophilic addition in the MALDI-ToF-MS analyses. The presence of the nucleophilic addition reactions can explain discrepancy between the ^{1}H-NMR and GPC results regarding acrylates conversion and monomer content. The base reacted monomers could exhibit similar retention times in GPC similar to those of unreacted monomers. MALDI-ToF-MS analyses reveal that these bases also react with the higher molecular weight LCOs. The total concentration of these species is expected to be around 6 mol%, which should not exceed the initial concentration of the base catalyst in the reactions. In contrast, TEA follows purely base-catalysed thiol-Michael addition pathway. Different from previous cases, the presence of only EDDET reacted MMs and DMs can also explain the disagreement between GPC and ^{1}H-NMR analyses for TEA. However, our investigation highlights that TEA uniquely enables nucleophilic addition free thiol-Michael addition without side reactions albeit at the cost of lower conversion.

Among these four catalysts, in order to avoid side products in thiol-Michael addition reaction, results suggest that a tertiary amine such as TEA should be used. Besides the nucleophilic addition, the GPC and MALDI-ToF analyses of DBU reacted sampled shows a clear indication of a cleavage reaction. To prove the case, we have done additional experiments with non-reactive mesogenic units (NRM) sharing the same core molecular structure as DM (**Figure S31**). We found that only in the case of the DBU catalysed reaction extra 1H-NMR signals were observed (**Figure S32**). One of these signals correspond to the presence of a carboxylic acid proton in the sample, indicating a cleavage of aromatic ester bond due to DBU.

We also experimented with a non-reactive widely used chiral dopant and found that for DBU, DPA, and α-MBA there were extra peak formation in ^{1}H-NMR analyses that could indicate presence of a cleavage when there are sequential aromatic ester bonds (**Figure S33-S38**). These extra peaks were more significant in the presence of EDDET as the proton donor reactant, which suggest a cleaving reaction. Since TEA was promising as a highly selective thiol-Michael addition base catalyst, to improve the overall conversion, alternative aprotic solvents like acetone, and DMF were investigated[3]. However, no significant improvement was observed by using different aprotic solvents (**Figure S39**). On the other hand, increasing the TEA concentration to 10.0 mol% and doubling the overall reactant concentration in DCM by halving the solvent volume led to a marked improvement in reaction yield. ^{1}H-NMR analysis of the concentrated TEA catalysed reaction showed a conversion of 95 mol% in the thiol-Michael addition reaction after 24 h (**Figure S40**). We did not observe extra peak formation or unusual peak shifts in the ^{1}H-NMR after increasing the overall concentration and hence we do not expect the aforementioned side reactions present in this batch. The GPC analysis of this concentrated reaction also supports the MALDI-ToF-MS findings that TEA catalysed reaction batch also included some thiol-end oligomers, which are going to continue to grow with DMs or to be end-capped with MM.

Based on the above findings we prepared LCEs (LCE_{DPA}, LCE_{TEA1}, $LCE_{TEA2)}$ using 3 eq. of DM, 2 eq. of EDDET and DPA (6 mol.%) or TEA (6 mol.% or 10 mol.% with doubled concentration) as base (**Figure a**). After the thiol Michael addition reaction, the solvent and free base were evaporated at room temperature, overnight. ^{1}H NMR spectroscopy revealed the presence of acrylate endcapped oligomers with degrees of polymerization 3.44, 2.20, and 3.05, for oligomers used for LCE_{DPA}, LCE_{TEA1}, and $LCE_{TEA2,}$ respectively (**Figure S42-44**). MALDI-ToF-MS analyses again revealed the formation of nucleophilic base adducts as side products but only when DPA was used as a base (**Figure S47**). The degree of polymerization of LCE_{TEA2} agrees well with the feed ratio, assuming high conversion (vide supra). For LCE_{TEA1}, a lower degree of polymerization is observed, possibly due to incomplete thiol-Michael addition reaction, while LCE_{DPA} exhibits higher degree of polymerization compared to LCE_{TEA2} which may be attributed to the formation of DPA-adduct products (vide supra). Subsequently, the oligomers were photopolymerized in the presence of photoinitiator, to fabricate the LCEs [27]. DMTA of the LCE_{DPA}, LCE_{TEA1}, and LCE_{TEA2} showed different storage (G') a

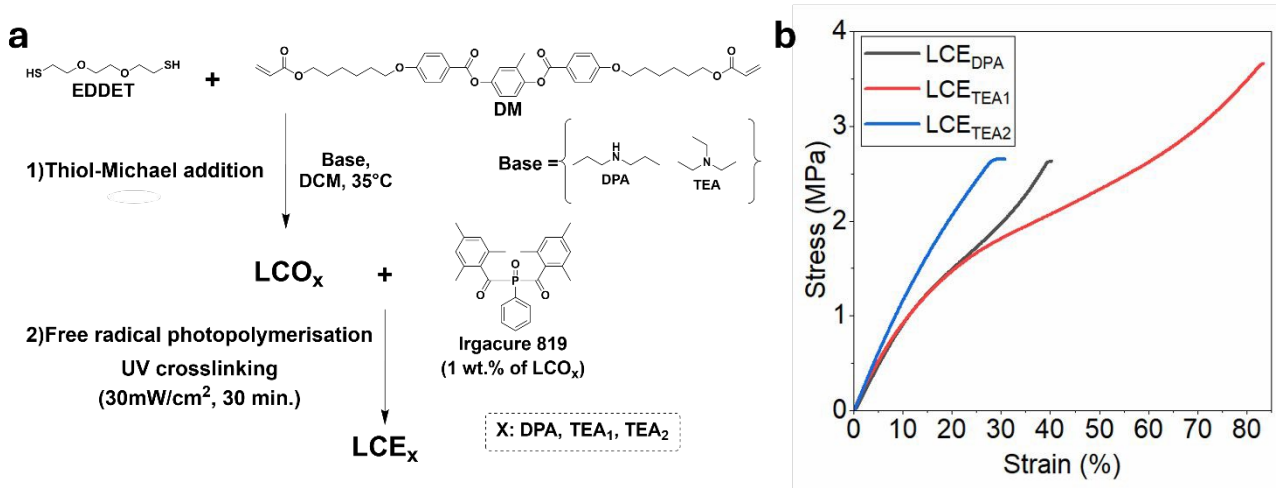

Figure 4 a) Schematic of the model reaction to prepare LCEs. X represents the base used in thiol-Michael addition. b) Stress-Strain analyses of LCE_{DPA}, LCE_{TEA1}, and LCE_{TEA2}.

values of 48.9 MPa, 34.5 MPa, and 32.4 MPa, respectively (**Figure S48**). The same trend was observed for loss modulus (G''), with values of 18.6 MPa, 12.1 MPa, and 9.7 MPa (**Figure S49**). The Young's modulus (E) values for the LCEs were determined as 12 MPa, 10.0 MPa, and 9.4 MPa for LCE_{TEA2}, LCE_{TEA1}, and LCE_{DPA}, respectively. The stress-strain data indicates that the LCEs become stiffer and mechanically stronger when moving from LCE_{DPA} and LCE_{TEA1} and LCE_{TEA2}. The crosslink density is most likely the highest in LCE_{TEA2}, as it contains the highest concentration of acrylate groups prior to the crosslinking step. In contrast, LCE_{DPA} exhibits a lower crosslink density due to the formation of base-adduct products. In case of LCE_{TEA1}, the unreacted EDDET resulting from the incomplete thiol-Michael addition may act as a chain-transfer agent in the second photopolymerisation step, thereby reducing the effective crosslink density. These differences in crosslinking density are supported by the stress-strain behaviours of LCE_{DPA} and LCE_{TEA1}, showing typical "flow" characteristic, whereas LCE_{TEA2} exhibits no flow behaviour (**Figure b**). These data show that the catalyst (type, concentration) plays a decisive role in determining the mechanical properties of LCEs.

Conclusions

This study demonstrates that apart from TEA, three commonly used bases in preparing LCO and LCEs lead to the formation of nucleophilic base adducts as side products as identified with MALDI-ToF-MS analyses. Although thiol-Michael addition is regarded as a highly selectivity reaction, careful consideration of the choices is essential to achieve maximal selectivity. We attribute the absence of nucleophilic addition in case of TEA to its tertiary amine structure. However, this advantage comes at the cost of a lower overall conversion in thiol-Michael addition. The conversion could be significantly improved to 95% by increasing the TEA catalyst concentration to 10 mol.% of the reactants and the overall reactant concentration was set to approximately to 0.5M. The DMTA analyses of the LCE_{DPA}, LCE_{TEA1}, LCE_{TEA2} indicate that both the type and the concentration of the catalyst used in thiol Michael addition directly influence the mechanical properties of the resulting LCEs.

Our results indicate that previous synthesized LCOs and LCEs prepared via base catalysed thiol Michael addition may contain base adduct impurities. Consequently, the effective crosslink density may differ from the intended design as supported by the demonstrated LCEs. Overall, this work provides practical guidelines for the preparation of LCO and LCE which might ultimately enhance the performance of the resulting stimuli responsive materials and devices by enabling greater control over the thiol Michael addition reaction.

Author contributions

R. Umut Dinc: writing – original draft; conceptualization (equal); investigation; visualization; and writing – review & editing (equal). **Johan Lub**: conceptualization (equal) and writing – review & editing (supporting). **Xianwen Lou**: investigation (supporting). **Augustinus J. J. Kragt**: supervision (supporting); conceptualization (equal); and writing – review & editing (supporting). **Albert P.H.J. Schenning**: funding acquisition (lead); resources (lead); conceptualization (equal); supervision (equal); and writing – review & editing (supporting).

Conflicts of interest

There are no conflicts to declare.

Data availability

The electronic supporting information (ESI) document including characterization, equipment, and additional analyses and graphs is available free of charge on the Royal Society of Chemistry Online website. The database of this publication is available free of charge at https://doi.org/10.5281/zenodo.19679221.

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Data availability

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