Liquid crystalline vitrimers for renewable functional actuators

State-of-the-art and Objectives

Liquid crystalline elastomers (LCE) make a remarkable class of materials. At their inception in the 1980s, LCE represented a mere curiosity, but two events in the early 1990s have turned LCE into one of the hottest topics of international multidisciplinary research and development: Finkelmann (in Germany) started working with silicones, making the low glass transition elastomers (rubbery in the ‘human’ temperature range), and learned to make monodomains (large samples with uniformly aligned orientational anisotropy). At the same time, Warner and Terentjev have developed a complete theory of LCE state and mechanics. After this, meaningful experiments on LCE with controlled alignment became possible – and the good theoretical understanding of the processes guided these studies. As a result, the field has ‘exploded’, and today there are dozens of strong research groups in EU, USA, Japan, China, Russia, India, Brazil, Mexico, etc. publishing hundreds of research papers a year. The 16th biannual International Conference on LCE will run in Houston, TX, with several hundred participants, with a programme solidly focused on LCE applications.

One of the two key theoretical predictions about LCE was their ‘equilibrium actuation’ (the other being the ‘soft elasticity’: an equally remarkable topic, also promising many unexpected applications). Finkelmann has soon confirmed this effect, and then a systematic study of Tajbakhsh and Terentjev has established how the degree of microscopic polymer chain anisotropy affects the spontaneous and fully reversible change of sample length. This elongation ratio $L/L_0$ is called the ‘actuation stroke’, and the illustration shows that it changes continuously in proportion to the temperature change below the isotropic transition point, with the maximum stroke of 50% for the lowest curve – and up to 250% for the highest curve (the materials in that study differed in the fraction of added main-chain polymer, increasing the average local anisotropy; this change also shifts the isotropic transition point). In order to evaluate mechanical work done by such an actuation cycle (heating-cooling in this case), there has to be a load (stress) applied, and the illustration shows one representative LCE doing mechanical work of $\sim 150$ kJ/m$^3$ per unit volume (evaluating the full work would be misleading, because $W=force*displacement$, and the displacement depends on how long the initial sample was: you can have as large work $W$ as you want by lifting the same weight by a longer strip of LCE). Our long experience with LCE tells that these materials can only withstand the maximum stress of $\sim 100$ kPa before breaking (both in tension and in compression), so the maximum mechanical work per unit volume cannot exceed $\sim 50$ kJ/m$^3$ for an elastomer with a 50% actuation stroke as an illustration. It is important to emphasize the equilibrium nature of LCE actuation: it is the natural length of the sample that is changing, and so the process can repeat over as many cycles as needed – it is only the applied load that may lead to degradation.

It is also important to note that the majority of modern literature on LCE actuation is focused on bending (rather than linear tensile tests described above). For the simple reason: in bending, when one side of the sample contracts with respect to the opposite, one can achieve a very large amplitude of motion by very little input; the mechanical work in such a bending cycle would be close to zero. So many spectacular results on

bending actuation\textsuperscript{6} are perhaps interesting for signal guidance, or surface reflectance – but certainly not for any mechanical application.

The Warner-Terentjev theory makes it clear that the reason for mechanical actuation is the change in the orientational order of molecules, which are well-aligned (monodomain) and are crosslinked into a dense network. Both Finkelmann and Terentjev have quickly realised that one can change this order not just by changing the ambient temperature (as people do in ordinary liquid crystals), but also by light – if the molecules making the network contain photo-responsive groups.\textsuperscript{7} This started a new wave of excitement in LCE actuators: now you could induce a large mechanical action fast, and without contact, just by shining a light on the elastomer.\textsuperscript{8,9} There are two mechanisms behind photo-actuation: a direct release of heat on light absorption, which causes local change of orientational ordering for entropic reasons – and a more delicate effect when the photo-absorbing molecule is an anisotropic rod itself, and undergoes photo-isomerisation disrupting local orientational anisotropy (azobenzene derivatives) by altering the potential energy of anisotropic interaction. Initially the two were confused, but later these mechanisms were clearly separated,\textsuperscript{9} and now a much preferred (far more robust) method is the first: one can select specific dyes that are more efficient in releasing heat, and absorb in a required spectrum range, and disperse them in the LCE actuator to enable its photo-response. Our long experience shows that carbon nanotubes and graphene nanoplatelets are the best in converting broad-spectrum light into local heat – while the laser welding dyes like isocyanine green are best to convert narrow-band near-infrared light into high local heat\textsuperscript{10} (while azobenzene derivatives have a narrow-band UV absorption).\textsuperscript{7} The illustration (data from\textsuperscript{10}) shows the ‘light ON’ – ‘light OFF’ cycles on a typical LCE doped with a standard commercial dye (not optimised for the photo-actuation), pointing the repeatability of response, and the dependence on light intensity. The speed of response has been shown to be determined by the rate of absorption saturation in a material (faster in thinner samples), and could be made to fractions of a second.

The speed of actuation response, the magnitude of actuation stress (on length-fixed sample) and the stress-strain-power values make LCE the material that matches the human muscle parameters almost exactly. The illustration of ‘Actuation Map’ (from a review\textsuperscript{11}) shows where the range of LCE actuators sits comparing to many other systems used in technology. The ability to initiate the mechanical action by light adds to the attractiveness of the material; other stimuli (i.e. methods of changing the local orientational order) have also been demonstrated – by solvent intake or by magnetic heating when ferrous nanoparticles are dispersed. However all these effects rely on the fact that LCE is formed as a monodomain – and since Finkelmann’s work there is no other practical method to form a uniformly aligned crosslinked elastomer than by his two-step crosslinking process\textsuperscript{2,4}.

The two-step crosslinking-alignment process relies on the separation of time scales. Once the polymer solution is prepared, crosslinking is initiated and the system is allowed to form a weak gel. Once in this state – a mechanical deformation is applied (usually a uniaxial tensile stress), during which the polymer chains that are already crosslinked develop a specific uniform stress-induced anisotropy. At this point the final full crosslinking is applied ‘freezing’ this anisotropy in the network. Now when a LC order is formed, it does not choose random directions, but is guided by the frozen anisotropy – and forms a clean uniform monodomain sample. This is the best process leading to what is called “isotropic genesis LCE”, where the sharp phase transition occurs (see illustrations above) and the best ‘soft elasticity’ is found\textsuperscript{5,12} (when the stretching and

\textsuperscript{11} Huber, Fleck and Ashby (1997) Proc. R. Soc. Lond. A 453, 2185
second crosslinking take place in the LC phase, and the domain walls get ‘frozen’ in the material, leading to a dispersion of the transition point, lack of soft elasticity in the “nematic genesis LCS”). Unfortunately, this two-step process fundamentally cannot produce anything except a flat strip (or a thick fibre): the weak gel at the first stage does not permit complex shape formation – if that first stage is carried to a stronger gel, then no good LC alignment and actuation can occur, because it is the non-crosslinked chains that will be made in anisotropic conditions and lead to the final order and actuation. This ‘bottleneck’ is the reason why there are no spectacular applications of LCE on the market. This is where the field is now: LCE offer a great promise, remarkable opportunities – yet for a technical reason their best applications remain practically non-viable.

**This proposal aims to change this status quo, and open the road for these new applications.**

There have been three experienced chemists, who worked with Terentjev over the years, trying to first understand these issues, and then find a solution to them: Tajbakhsh has since then retired (as has Finkelmann in Germany), so the initial LCE synthesis expertise was lost; however, for the last few years, two talented PDRAs have learned much from Tajbakhsh: Ji is now a Professor in Tsinghua University (Beijing) and Marshall is now a Senior Scientist in a chemical company Domino Printing that produces functional polymers. Both have continued joint work with Terentjev on LCE materials – and finally, in 2013, we had a breakthrough.

We always understood that an alternative solution to the ‘two-step crosslinking’ protocol was needed, which could only come from a concept of *thermoplastic elastomers*: networks that are crosslinked dynamically and that could be re-moulded at a high temperature into complex shapes. All modern polymer industry uses this thermoplastic concept: from shoes to aircraft. We have tried many things over many years (in LEAPFROG project – the polyurethane concept, in NOMS project – the thermoplastic block-copolymer concept), and grew to understand that it cannot work. The reason is that for actuation we need to release a lot of heat internally, which inevitably disrupts the thermoplastic matrix and undermines the mechanical strength of the material: fundamentally such actuators will show creep after many cycles. It is good to demonstrate interesting effects for a few cycles, but is not useful for real industrial applications. So when Ludwick Leibler (ESPCI, Paris) has announced their new idea of *vitrimers*\(^{13}\), we knew this is our ‘ticket’. Unlike in usual thermoplastic networks, which have their dynamic crosslinking increasingly disrupted on heating, in a vitrimer the number of covalent bonds holding the network together remains constant at all times. But the rate of a bond-exchange reaction (BER) increases on heating, in a very sharp manner since high energy barriers are involved, which allows the material to become malleable: easy to pressure mould above the ‘vitrification temperature’ \(T_v\) (which is often 130-180°C or could be higher). Yet the differential stiffness and the structural integrity are not compromised, since the crosslinking bonds exchange, but do not reduce in number. An example of transesterification BER is illustrated here, showing how two polymer chains [a-b] and [A-B] can reconnect into a different topology [a-A] and [b-B] above \(T_v\). In a material under stress, this change will induce a plastic flow, and thus enable re-moulding. We followed Leibler’s ideas and formed such BER polymer networks with liquid-crystalline (rod-like) molecules – and named these liquid crystalline vitrimers xLCE, for ‘exchangeable LCE’\(^{14}\).

Many positive improvements were found in the early xLCE systems: the much improved robustness and higher modulus while still in the rubbery regime (which lead to higher stress allowed, and much higher mechanical work on actuation), the demonstrated ability to re-mould existing samples into new shapes without loss of mechanical/actuating properties, and crucially – the ability to align and form the uniform monodomain, by manipulating tensile stress and temperature between \(T_v\) and the isotropic phase transition \(T_i\) of the liquid crystal (the details are described in the original paper\(^{14}\)).

However, these early xLCE materials were not perfect: mainly, they did not have the nematic phase, but a smectic A phase instead, which has many disadvantages: the smectic LCE phase is very stiff, with additional

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\(^{13}\) Montarnal, Capelot, Tournilhac and Leibler (2011) *Science* 334 965

\(^{14}\) Pei, Yang, Chen, Terentjev, Wei and Ji (2014) *Nature Mater.* 13 36
internal constraints due to the layer confinement \(^{15}\) – something may be useful for multiple shape memory effects \(^{16}\), but not for our intended ‘classical’ applications. For the last 3 years, Terentjev and Ji have worked to improve their xLCE materials: primarily to obtain a single nematic liquid crystal phase between Ti and the glass transition temperature Tg, but also to make Tg lower so that the xLCE material is elastic at the ambient temperatures – and make Ti lower so that the main range of actuation is closer to the ambient temperature. This has now been achieved by using a mixture of different mesogenic monomers, which preserves the orientational order but disrupts the smectic layering, and by using siloxane segments as spacers to lower the Tg (see illustration; the papers are in press); we also now use a different BER (allyl sulphide), which we feel is better. The xLCE materials are now ready for the next step: use them in smart-technology applications, which is the objective of this proposal.

These objectives are divided into two distinct parts of the workplan: Part A is the chemistry-led element, where we will work to optimise the new xLCE structure for each target application. It needs a lot of innovation in itself, and several major challenges to face (details below), but its ultimate role is to provide a sufficient amount of photo-actuating xLCE material with required parameters for the use in target applications.

**Part A, WP1: Optimisation of nematic xLCE composition**

The aim is to have the robust, and ideally simple, chemistry, leading to the nematic LC polymer chains, which will be crosslinked by a bond-exchange reaction into the xLCE network. There are three key temperatures that determine the viability: the vitrification point Tv (above which the material shape can be re-moulded without any loss of functionality), the nematic-isotropic transition point Ti (below which the LCE network displays the mechanical actuation), and the glass transition point Tg (below which the material becomes a brittle solid and no actuation can occur). The latter point (Tg) may instead be a point of polymer crystallisation – either way, the material becomes a rigid solid.

Depending on the application, it may be that Tg has to be far below the ambient temperature, if the application utilises the dynamics and needs a rubbery response – or slightly above, if the application utilises the rigid shape that is set by the processes at higher temperature. Our approach to manipulate Tg is by using the siloxane spacers between mesogenic monomers, using the hydrosilation reaction to bond with di-vinyl mesogens. This chemistry is very familiar to us: we learned it directly from Finkelmann, and have been using in our lab since 1998 (we have good experience with choice of catalysts, and reaction regimes). The fraction of siloxane in a polymer chain is known to suppress the glass transition (a pure siloxane may have Tg as low as -70-80°C, but with a small fraction we are likely to have Tg just below 0°C).

An alternative, which we have tried before (trying to make LCE fibres under LEAPFROG), is to use polyurethane chemistry and have polymer chains by combining mesogenic diols with di-isocyanate spacers. This class of materials also has a low Tg, and good mechanical properties, but for us it is less familiar chemistry and so it will be an optional extra in the present planning.

The control of the nematic-isotropic transition temperature is achieved in two ways. The coarse point of the transition is


determined by the proportion of the 2-ring and 3-ring monomers, the latter pushing the Ti up to above 100-110°C. A more fine control will be exerted by dopants: we will need the photochromic dye (or nanoparticles) dispersed in the matrix, which naturally lowers Ti. Working with these parameters, the wide range of operating temperatures Tg–Ti will be achieved.

It is vital that the vitrification temperature Tv is much higher than Ti, so that operating temperature range of actuation (even local, when nanoparticles release their heat) does not cause the plastic flow, and the material shape stays robust for many T-cycles. We will work with two BER classes (transesterification and allyl sulphide exchange) and in both cases the vitrification point is controlled by the catalyst content – which is going to be our approach. The illustrative plots, combining DSC and thermo-mechanical studies, show how the temperature ranges were distributed in our early xLCE materials (Tg and Ti were too high, but the graphs illustrate the principles).

The tasks under this WP are: assuring nematic and glass phases in the relevant T-regime, settling on the bond-exchange crosslinking strategy, and sensitising the material with suitable photochromic dyes for photoactuation. This is a key WP for the first year of the project, because the xLCE material produced will enable the work under Part B (application development). But I have a reasonable expectation that this will succeed fast, because of the extensive preliminary work that we did with Yan Ji and her students in the last 3-4 years. Our chemistry lab is well equipped, with 4 fume cupboards and 4-6 benches allocated to this project (this is more than a ‘normal’ Chemistry Department lab would have, because our ‘wet lab’ space in Physics is not contested – and we were building this synthesis capacity for many years).

### Part A, WP3: xLCE nanocomposites and photo-sensitivity

Sensitising the xLCE material with photochromic dopant in order to achieve the photo-actuation response needed for a particular application is a delicate task, depending on continuous constructive interaction with the Part B of this project. For instance, the sunlight-actuated motor and the heliotracking device require a response to the broad spectrum of illumination, while microfluidic and tactile display technologies are likely to require narrow wavelength actuation (ideally away from the visible spectrum range). There is a wide variety of dyes available, and we have worked with many in the past, getting experience in which dyes achieve what effect.

Two systems in particular are the most promising for our planned applications. Carbon nanoparticles (short segments of single- and multiwall nanotubes, and graphene nanoplatelets) have a very broad spectrum of absorption – and are known to release an enormous heat on illumination (cf. self-ignition effect of CNT). Dispersion of carbon nanoparticles in polymer matrix is challenging for many, since the ‘usual’ methods of using surfactants are not optimal in our case: we do need exposed π-electrons to achieve the required light-heat conversion (although we found that with multiwall CNT the demand for outer surface π-electrons is reduced, as they show strong broadband absorption even when covered with a surfactant). It happens so that our group is one of the world leaders in this dispersion technique, including the process of controlled cutting of nanotubes into short segments, designing specific new surfactants that work with carbon nanoparticles in a specific polymer matrix, and understanding the process of dispersing carbon nanoparticles in a hydrophobic matrix; this expertise is on record in papers and reviews.

The isocyanine green dye (ICG) is specifically designed to release heat on near-infrared light absorption (hence its wide use in laser welding of plastics); it absorbs at ~800nm which is easy to achieve by commercial lasers – it is also safe for humans (unlike UV required for other promising dyes) and is therefore widely used in medical treatment. The illustration shows the spectrum of ICG in solution, and when dispersed in the xLCE film, demonstrating that the dispersion did not alter the ICG electronic structure and absorption properties. The analogous absorption spectrum of carbon nanoparticles is, of course, completely

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17 Pritchard, Redmann, Pei and Terentjev (2016) *Polymer* **95** 45
19 Loomis, King, Burkhead, Xu, Bessler, Terentjev and Panchapakesan (2012) *Nanotechnology* **23** 045501
flat between 400–950nm (as they are ‘black’).

The demonstration plot of an unpublished pilot study of photo-actuation of xLCE with ICG (illuminated by 800nm defocused laser LED) illustrates several key facts that reassure us about the whole project feasibility. There is a strong intensity dependence, which promises a good analogue response. There is stability on the ON-plateau, which means the sample ‘holds the tensile force’ well. The actuation stress (for the sample illuminated at fixed length) is enormously higher than in the old LCE photo-actuators. The actuation time of ~10s may appear slow (although it is very adequate for some of the applications), but that time is controlled by the thickness of the active film, which in this pilot case was ~0.5mm (can be thinner in many applications, and the response – faster).

The fact that dispersion of ICG did not appear to cause electronic interactions is reassuring, however, there is always a strong possibility that photo-chromatic materials would have a strong interaction with free radicals, and thus their presence would adversely affect the chemistry (polymerisation or crosslinking) if the radicals are involved. This is a risk, and we have several ideas to deal with this issue (apart from simply adding the dye after all reactions have been completed, which is the fall-back), but this will be a serious work for two chemists.

The task under this WP is to establish an on-demand production of chemically stable nematic xLCE material with homogeneously dispersed carbon nanoparticles / ICG, at concentrations optimised for the required application.