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Room Temperature Dynamic Polymers Based on Diels–Alder Chemistry

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Dedicated to Professor Roeland Nolte on the occasion of his 65th birthday

Abstract: Dynamers based on reversible Diels–Alder chemistry have been obtained and shown to undergo dynamic exchange at room temperature. Their study in solution by small-angle neutron scattering indicated the formation of long and highly flexible chains. Polydispersed molecules gave T_g values below room temperature, permitting the generation of a dynamic elastomer upon introduction of a dynamic cross-linking agent. The use of a system with a low equilibrium constant gives access to materials with interesting self-healing properties.

Keywords: Diels–Alder reaction · materials science · polymers · reversible cross-linking · thin films

Introduction

Dynamers are a class of polymers of either supramolecular or molecular nature that are generated from monomers linked by reversible connections, that is, non-covalent interactions or covalent bonds formed through reversible reactions, respectively. They represent dynamic materials.[1,2] Considering covalent dynamers, this reversibility results in the possibility that, under suitable conditions, the bonds between monomers may dissociate and set free two new reactive chain ends, which may in turn react with any chain end presenting a complementary reactive functionality. This feature permits the polymeric chains to continually scramble their sequences through reversible cross-over. It also allows for the incorporation of new monomers into the structure, even if they are added after the initial synthesis of the polymer chain.

The implementation of this property to create dynamic/adaptable materials is a blossoming field of basic and applied research. The success of such a strategy relies, among other factors, on the properties of the reactive link between the monomers. The formation of imines or acylhydrazones has been successfully used to obtain dynamers that display interesting optical or physical properties.[3] Dynamers that display rapid exchange at room or physiological temperatures are of particular interest because they can find applications as biopolymers or drug-delivery systems.[4] We recently reported a system based on Diels–Alder chemistry that already displays dynamicity at room temperature.[5] It involved fulvenes as the dienes and dicyanofumarates or tricyanoethylenecarboxylates as the dienophiles, and may allow the generation of room-temperature dynamers.

The Diels–Alder (DA) reaction, among other cycloadditions, has previously been used to synthesise polymers.[6] It has found applications in the building of the main chain, the cross-linking of polymeric networks or the introduction of side chains,[7] all of which take advantage of its high chemoselectivity. The reversibility of the adduct formed during the reaction has been seen as rather a drawback because it makes thermal decomposition of the polymer possible. A few groups, however, have harnessed this property to create responsive materials and mendable polymers. A dianthracene–fullerene copolymer of thermally controllable length[8] was based on the thermal reversibility of this diene/dieno-

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phile pair.[9] Reversible dendrimers and surfactants based on the classical furan–maleimide pair were also found to be responsive to temperature.[10] These reactants have been used to build a polymeric material that was thermally remediable at temperatures well above room temperature.[11]

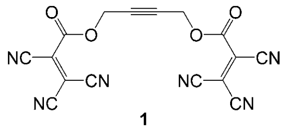
We investigated the use of the system based on room temperature dynamic DA chemistry, which we have described earlier,[5] to obtain dynamers that present chain scrambling at room temperature, a feature that may ultimately lead to a material able to self-repair at room temperature. It was recently shown that a supramolecular elastomer made of molecular components linked by non-covalent interactions displayed a capacity for self-healing at room temperature.[12] Specifically, this material incorporated cross-linking through hydrogen bonds. Such supramolecular polymers are by essence dynamic materials.[1,2] The development of dynamic covalent materials that may self-heal at room temperature was a major driving force for our present studies, as they can be expected to open the route to a wealth of interesting applications for such molecular dynamers.

The DA reaction is interesting in that it is an addition and not a condensation process. Hence, all atoms present in the starting components are also present in the product and it is therefore a self-contained dynamic system.[5] This feature allows for the reaction to be reversible without the use of an ancillary compound, catalyst or external stimulus. Also, exchange of the components of the chain of a dynamer based on DA chemistry may be regulated through temperature.

Results and Discussion

Synthesis of the materials

Dienophile and diene monomers: The study of such a system first required the synthesis of a monomer that presented either two tricyanoethylenecarboxylate or two dicyanofumarate moieties. Such molecules were unknown and their synthetic access is highly hampered by the high sensitivity of these functional groups towards nucleophiles, which renders their chromatography on silica or alumina gel impossible, for example. This problem was solved by using molecules that were designed to have a solubility high enough to allow the polymeric chains to remain in solution, but low enough so that they could be purified by precipitation. This led to the choice of bis(tricyanoethylenecarboxylate) **1** and bis(dicyanofumarate) **2** as synthetic targets.



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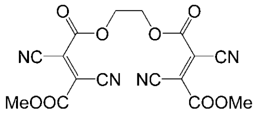

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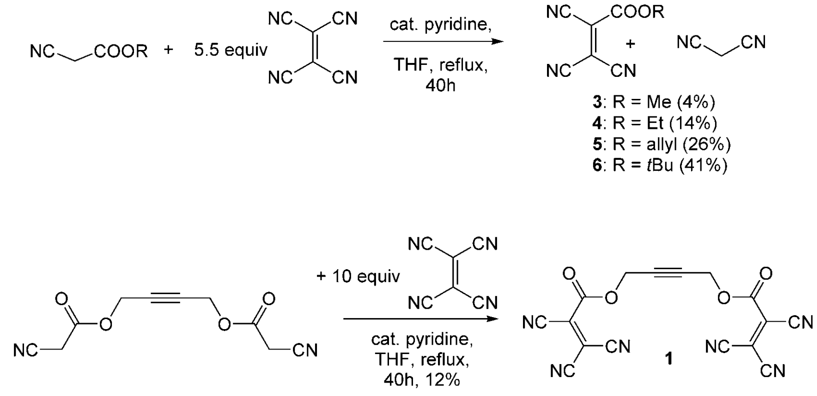
The synthesis of tricyanoethylenecarboxylates was accomplished through the treatment of tetracyanoethylene (TCNE) with cyanoacetate in the presence of a base, as described in the literature.[13] TCNE undergoes a Michael addition of the cyanoacetate anion generated by abstraction of one of the acidic protons by pyridine. This intermediate, stabilised by multiple cyano groups, can either reverse by ejecting the cyanoacetate anion or, after proton exchange, evolve by ejecting one molecule of malonitrile to form tricyanoethylenecarboxylate. But under the same conditions, this tricyanoethylenecarboxylate can undergo a second Michael addition of a cyanoacetate anion by following the same mechanism to generate dicyanofumarate. In each case, the driving force of the reaction is the formation of a less electron-deficient cyanoolefin. This is reflected in the reactivity that these strong dienophiles display when they are engaged in DA reactions. For 6,6-dimethylfulvene in a 100 mM solution of both starting materials in $CDCl_3$ at room temperature, the equilibrium constants observed by ^{1}H NMR spectroscopy were $>10^4\,\mathrm{M}^{-1}$ for TCNE (no sign of reactants left), $2350\,\mathrm{M}^{-1}$ for methyl tricyanoethylenecarboxylate and $99\,\mathrm{M}^{-1}$ for dimethyldicyanofumarate.[5] To minimise the formation of dicyanofumarate, an excess of TCNE had to be used. Cyanografted reverse-phase HPLC followed by Kugelrohr distillation[13] could not be applied because the distillation is only compatible with small molecules. We used a fractional precipitation method to first remove most of the excess of TCNE by adding heptane. The tricyanoethylenecarboxylate was then obtained by filtration after rendering the solution even more apolar. This process gave poor reaction yields. It was found that the more soluble in an apolar organic medium the formed tricyanoethylenecarboxylate was, the better the yield was. The yields ranged from 4% for methyl tricyanoethylenecarboxylate **3** to 41% for *tert*-butyl tricyanoethylenecarboxylate **6** (Scheme 1).

To obtain a bifunctional molecule that would serve as a monomer, we decided to use but-2-yn-1,4-diol as a linker between two tricyanoethylenecarboxylate moieties because the bis(dienophiles) obtained could be expected to have both

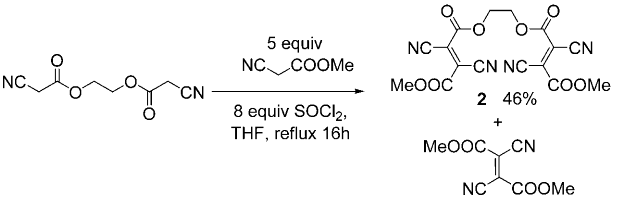
Abstract in French: *Des dynamères basés sur la chimie de Diels–Alder dynamique ont été obtenus et il a pu être montré qu'ils subissaient des échanges dynamiques à température ambiante. Leur étude par diffusion de neutron a montré la formation de chaînes longues et flexibles. La* T_g *inférieure à la température ambiante obtenue grâce à l'emploi de molécules polydispersées a permis la formation d'un élastomère dynamique, suite à l'introduction d'un agent de réticulation dynamique. Enfin, l'utilisation d'un système ayant une faible constante d'équilibre a permis d'obtenir un matériel avec des propriétés d'autoréparation intéressantes.*



Scheme 1. Synthesis of compounds **1** and **3**–**6**.

relatively good solubility in solvents of medium polarity and the ability to precipitate in media of low polarity. A further benefit was the extreme simplicity of its ^{1}H NMR spectrum, a desirable feature for a study of the reaction. The fractional precipitation method afforded **1** in 12 % yield (Scheme 1).

The synthesis of bis(dicyanofumarate) was achieved by treating a solution of methylcyanoacetate and ethylene glycol dicyanoacetate in a 5:1 ratio in tetrahydrofuran with an excess of thionyl chloride, adapting a procedure described in the literature.[14] The bis(dicyanofumarate) was less soluble than the dimethyldicyanofumarate and precipitated at the end of the reaction. Thorough washing with a mixture of chloroform and ethyl acetate gave bis(dienophile) **2** free of dimethyl dicyanofumarate in approximately 46 % yield (Scheme 2).

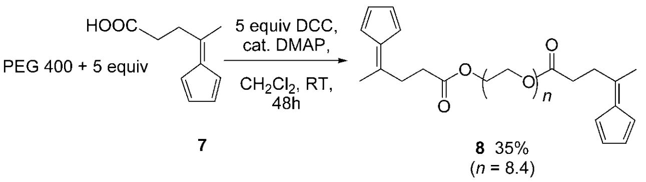


Scheme 2. Synthesis of bis(dicyanofumarate) **2**.

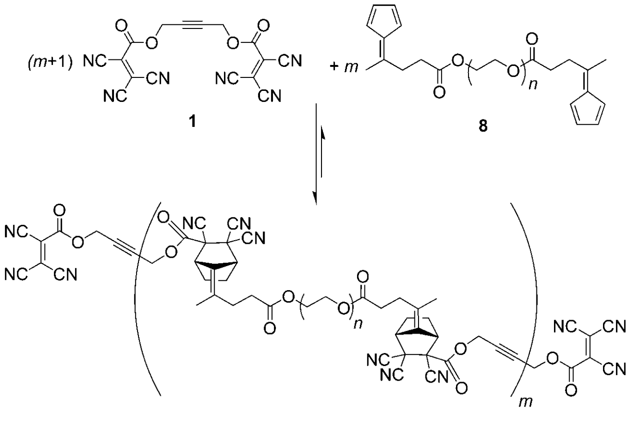
Bis(fulvene) dienes were obtained from 4-cyclopenta-2,4-dienylidenepentanoic acid **7** and α,ω-diols by using dicyclohexylcarbodiimide (DCC) as the coupling agent. Our first attempts with triethylene glycol were unsuccessful because the oligmers formed were poorly soluble. We then chose to use a polydispersed polyethylene glycol (PEG 400) to obtain long flexible monomers **8** of high solubility. The mean number of ethylene glycol repeat units between the two fulvenes was determined by ^{1}H NMR spectroscopy to be 8.4. The yield was 35 % after careful chromatography on silica to avoid the presence of monoreacted α,ω-diols (Scheme 3).

Generation of DA dynamers: With bis(fulvene) **6** and bis(tricyanoethylenecarboxylate) **1** in hand, we could begin studying the dynamers formed from these building blocks. The DA dynamers were generated by simply mixing the diene and dienophile components in a suitable solvent. Acetone turned out to be the solvent of choice, solubilising both bis(tricyanoethylenecarboxylate) **1** and the chains formed by reaction with bis(fulvene) **8** well enough.

Because any modification in concentration would affect their structure, the study of dynamers required analytical methods that are non-invasive and nondestructive. The equilibria were reached within a minute in solution at room temperature. This rather interesting feature turned out to increase the difficulty of the study, excluding for example studies by gel permeation chromatography or mass spectrometry.[15] ^{1}H NMR spectroscopy showed broad signals typical of polymers, but did not reveal information about the chain lengths. The speed of equilibration of the system did not permit the kinetics of formation to be tracked or destruction of the chain.[16] The structure of the DA dynamers obtained are shown in Scheme 4.



Scheme 3. Synthesis of bis(fulvene) **8**. DCC: dicyclohexylcarbodiimide, DMAP: 4-dimethylaminopyridine.



(**1**,**8**)

Scheme 4. Structure of dynamers (**1**,**8**) formed from **1** and **8**.

Characterisation of the DA dynamers by small-angle neutron scattering (SANS) studies

Small-angle neutron scattering (SANS) appeared to be an appealing method to study these DA dynamers in solution.[17] Its ability to give information at different length scales is a major benefit. In the dilute range, only small-molecular-weight polymers are expected to form because of the relatively low equilibrium constant, about 2000 M^{-1} for the model system.[5] DOSY experiments performed on dilute samples ($C=10$ mM) showed the formation of small oligomers. Therefore, a concentration of 100 mM for both starting monomers was chosen for the first attempt to ensure the formation of long enough chains.

Figure 1 displays the scattering pattern for a solution of the (**1**,**8**) dynamer formed by **1** and **8** in deuterated acetone at an initial concentration, C_0, of 100 mM and $T=20\,^{\circ}\mathrm{C}$. The scattering curve exhibits an overall behaviour characterised by the following sequence: a Guinier regime at a low q range associated with the finite size of the scattering objects, one intermediate regime in which the q dependence of the scattered intensity can be described by a power law with an exponent close to $-{}^{5}\!/_{3}$, followed by another power law regime with an exponent close to -1.

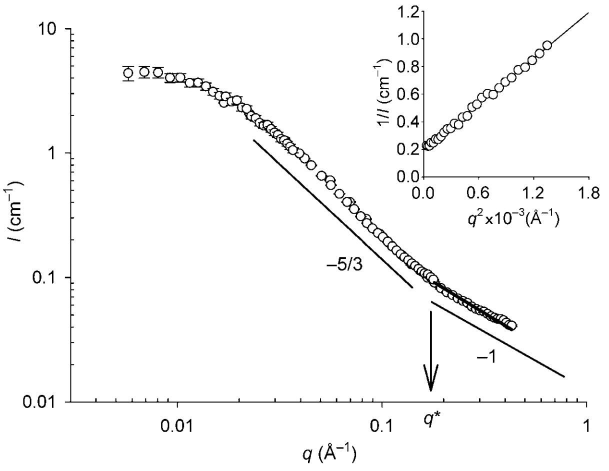


Figure 1. Scattered intensity as a function of q at $T=20\,^{\circ}\mathrm{C}$ (○) for a solution of dynamer (**1**,**8**) formed in deuterated acetone from **1** and **8** at an initial concentration of 100 mM (thick black line: des Cloizeaux fit). The inset graph represents the variation of $1/I$ as a function of q^2.

The data obtained at low q corresponding to large spatial scales can be fitted by the Ornstein–Zernicke law:

$$1/I(q) = 1/I(0)(1+q^2\xi^2) \tag{1}$$

in which ξ is the correlation length that represents the average mesh size of the transient network in the semidilute range, in which the polymeric chains are entangled. In the dilute regime in which the chains are far away from each other, ξ is given by $R_G/3^{1/2}$, in which R_G is the radius of gyration of the chain. The extrapolation to zero q of the scattered intensity, $I(0)$, provides a measure of the weight average molecular weight of the particle, M_w, for dilute systems or of the part of the chain forming the mesh $M(\xi)$ for entangled systems (see the Experimental Section for equations).

Figure 1 inset shows the plot of $1/I$ versus q^2 for the investigated sample. From the best linear fit of the data one obtains $\xi=53$ Å. The extrapolation of $I(q)$ to zero q gives $M(\xi)=29401\,\mathrm{g\,mol^{-1}}$, which corresponds to a degree of polymerisation, D_p, of about 29.

The intermediate regime corresponds to spatial scales such that $L_p \ll \xi$, in which L_p is the persistence length of the chain. In that regime one expects a power-law behaviour with an exponent μ, characteristic of the chain conformation ($\mu=-1$ for rigid particles, $\mu=-2$ for Gaussian chains and $\mu=-{}^{5}\!/_{3}$ for a chain with excluded volume interactions). The results of Figure 1 show clearly that the sample consists of chains expanded in a good solvent.

At large q values, $I(q)$ is controlled by smaller distances than L_p, over which polymers are rod-like, and we observe a crossover to an asymptotic q^{-1} dependence for the form factor $P(q)$, which is typical for locally rod-like structures. In this regime, where $I(q) \propto P(q)$, the data can be fitted by the des Cloizeaux equation:

$$P(q) = \frac{\pi}{qL_c} + \frac{2}{3q^2L_pL_c} \tag{2}$$

in which L_c represents the contour length of the scattering objects. The fit shown in Figure 1 (——) gives the following value for the linear mass density $M_L=29\,\mathrm{g\,mol^{-1}\,Å^{-1}}$. This value is in excellent agreement with the linear mass density of a single polymer chain, which can be estimated by using the monomer molecular parameters $m/a=1024.67/44=23\,\mathrm{g\,mol^{-1}\,Å^{-1}}$, in which m and a represent the mass and the length of the repeat unit, respectively (in brackets in Scheme 4).

The crossover value, q^*, between the intermediate excluded volume regime $q^{-5/3}$ and the rod regime q^{-1} permits the persistence length to be measured by using the following expression:[17a]

$$L_p = \frac{1.91}{q^*} \tag{3}$$

We have to keep in mind that Equation (3) is derived for Gaussian chains, however it gives our best estimate for the persistence length of the chains. One obtains $L_p \approx 11$ Å, that is, a value smaller than the monomer size characteristic of flexible chains composed of PEG units. The mean length of our repeat unit, comprised of 8.4 ethylene glycol units, was estimated to be about 44 Å.

The effect of the temperature on the scattering properties of the sample is illustrated in Figure 2. Within the experimental accuracy, the scattering curves superimpose on each other. The analysis of the low q data by using Equation (1) leads to the values of ξ and $M(\xi)$ given in Table 1. These re-

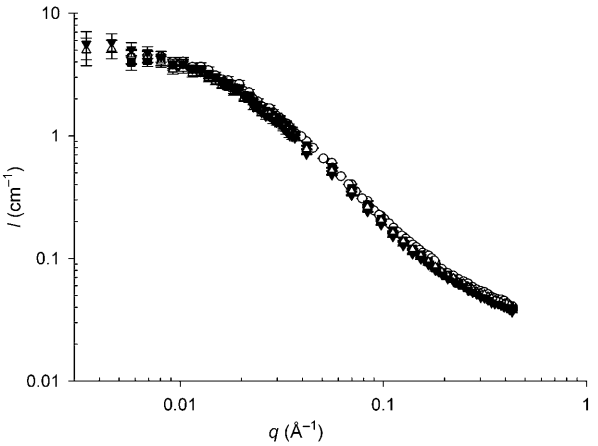


Figure 2. Scattering intensity versus q at ○: 20, ■: 31, △: 43 and ▼: 55 °C for a solution of dynamer (**1**,**8**) formed in deuterated acetone from **1** and **8** at an initial concentration of 100 mM.

Table 1. Physical parameters obtained from scattering data and fits at different temperatures for solutions of dynamer (**1**,**8**) formed in deuterated acetone from **1** and **8** at an initial concentration of 100 mM.

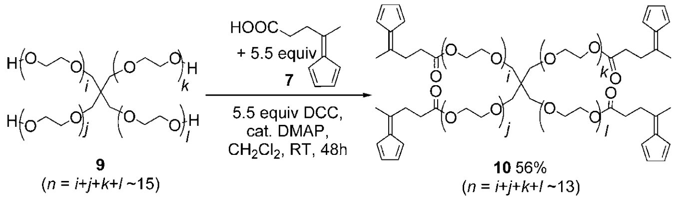
T [°C]	$I(0)$ [cm^{-1}]	ξ [Å]	$M(\xi)$ [gmol^{-1}]
20	5.107	53.0	29401
31	4.694	51.8	27024
43	4.610	52.9	26540
55	5.243	58.8	30184

sults indicate clearly that the chains are entangled because in the dilute regime one would expect a significant decrease in both ξ and $M(\xi)$ upon increasing temperature due to the dynamicity of the chains, whereas the correlation length in a semi-dilute solution is independent of temperature.

Formation and mechanical properties of thin films of dynamers (1,8) and (2,8)

The chains formed from bis(diene) **8** and bis(dienophile) **1** display high flexibility because L_p is smaller than the repeat unit length. Furthermore, the polydispersity of the polyethylene glycol used as a linker between the fulvene units ensured a T_g below room temperature, which prevented crystallisation of the formed polymer. The combination of these two properties allow one to envision the preparation of elastomeric materials with specific properties linked to the dynamicity of the systems. As previously performed in our laboratory for other covalent dynamers,[3e–g] we investigated the dynamic and mechanical properties of the present materials in a thin film. Such studies permit us to observe the integration at a macroscopic level of the dynamicity at the molecular level. In addition to bis(tricyanoethylenecarboxylate) **1**, bis(dicyanofumarate) **2** was used because we expected that the lower equilibrium constant of its interaction with fulvene would ensure a higher fraction of reactive chain ends in the material.

When a solution of **2** and **8** in acetone was evaporated under reduced pressure and elevated temperature, only an oily material was obtained. Interestingly, a qualitative increase in the viscosity was observed upon cooling to room temperature. The formation of an elastomer was tested by introducing multifunctional cross-linking agents. A tetrafunctional dynamic cross-linking monomer, **10**, was obtained by tetra-coupling of carboxylic acid **7** to pentaerythritol ethoxylate derivative **9** (Scheme 5).



Scheme 5. Synthesis of cross-linking agent **10**. The difference between the number of ethylene glycol units in **9** and **10** arises from displacement of the population size during the chromatography.

The use of **10** happened to be a key factor. Evaporation of a solution of **10** with two equivalents of **2** yielded a stiff thin film that recovered its initial shape after bending. Blending of **8** and **10** (3:1 or 4:1) with the corresponding amount of **2** (five or six equivalents, respectively) yielded soft elastic films (see pictures in Figure 3). The amount of residual solvent was negligible. Their yellow colour was an indication that unreacted fulvene chain ends were indeed present in the film, ready to react. Similar properties where obtained when **1** was used instead of **2** (Table 2).

Figure 3. Thin films based on Diels–Alder chemistry, obtained by blending a) **2** (1 equiv), **8** (0.6 equiv) and **10** (0.2 equiv) and b) **2** (1 equiv), **8** (0.8 equiv) and **10** (0.1 equiv).

The qualitative evaluation of mechanical features revealed an interesting property. After the film was elongated for a few seconds, it nearly recovered its initial shape on being released but remained slightly longer in the direction in which the elongation had been performed. A reason why this dynamic elastomer did not return to its initial position may be due to another route of stress relaxation. In a classical elastomer under elongation, the cross-links deter the chains from slipping apart from one another, forcing them to adopt an elongated conformation in the direction of the constraint (Figure 4). As the number of conformations the polymer can adopt is smaller in its elongated state, it results

Table 2. Qualitative properties of the films obtained by blending **1** or **2** with **8** and **10**.

Bis(dienophile)	Oligo(diene) [equiv] **8**	**10**	Property
1	1	0	oily
1	0.6	0.2	elastic
1	0.8	0.1	elastic
2	1	0	oily
2	0	0.5	stiff
2	0.6	0.2	elastic
2	0.8	0.1	elastic

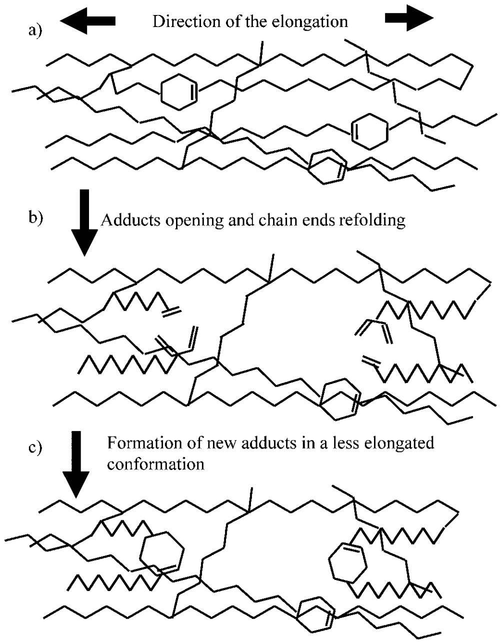


Figure 4. Scrambling of the chains leading to the relaxation of the elongation: a) chains in elongated conformation following the stretching of the film, b) opening of the Diels–Alder adducts and refolding of the chains and c) reaction of the chain ends to form a relaxed network.

in a loss of entropy, which is responsible for the observed force opposed to the elongation, according to Equation (4):

$$F = -T\left(\frac{\partial S}{\partial x}\right)_{T,V} \tag{4}$$

in which x is the length of the polymeric sample.

In the present case, the main difference from a classical elastomer arises from the continuous scrambling of the chains. Under the constraint of elongation, the opening of the DA adducts the chains are built from permits another relaxation pathway. After the opening of a DA adduct, the part of the system that was previously linking two cross-linking points generates two new chain ends that are able to adopt a less elongated conformation before finding a new complementary chain end. This mechanism should account for the formation of a less constrained network, that is, the dynamicity of the system leads to an evolution of the material driven by the elongation of its macromolecular structure. This effect represents a further illustration of the adaptation of dynamic materials to physical effectors (temperature,[18] electric field[19]), in the present case to *mechanical* stress.

We then carried out a self-healing experiment. Soft films of dynamers (**2**,**8**) were cut into two pieces, then these pieces were laid on top of each other and pressed gently to ensure a microscopic contact; only ten seconds after this the two pieces could no longer be separated by pulling them apart, but reacted to the constraint by elongating themselves (Figure 5).

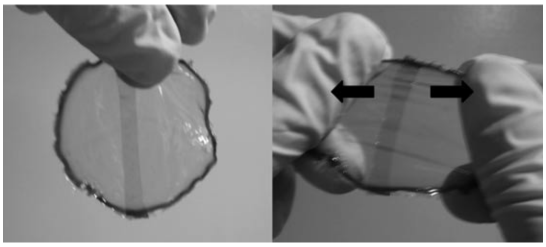


Figure 5. A thin film of dynamer (**2**,**8**) based on Diels–Alder chemistry after self-healing (left) and under elongation constraint (right). The darker rectangular region in the centre is the area where the two pieces were superposed and the self-healing took place.

This happened equally well with two parts of same composition or of different compositions using the two types of bis(dienophile). It is important to mention that the films were not sticking to anything other than themselves. This impressive property should, as it was designed for, come from the ability of the material, upon opening of the DA adducts, to form new polymeric chains/networks across the physical frontiers between the two parts. This behaviour is reminiscent of that described for supramolecular polymers,[12] which are intrinsic dynamic materials.[1,2] However, one important difference has to be mentioned; in the present case, self-healing takes place between the surfaces of the films, not only at the freshly cut surfaces. The surface of the film represents an area at thermodynamic equilibrium, as a result of low equilibrium constants for the interaction between the fulvenes and the cyanoolefins used. The constants are high enough to permit the formation of a material made of small molecules and low enough to allow the scrambling of the chains to take place even in the condensed phase. Consequently, the dynamer constantly creates new chain ends and forms new connections, thus building a material that can self-repair across all its volume.

Conclusion

The present work demonstrates the possibility of implementing a dynamic system based on the Diels–Alder chemistry we described earlier[5] for the generation of dynamic polymers. The use of long and polydispersed polyethylene spacers allows one to obtain highly flexible polymeric chains in solution, as observed by small-angle neutron scattering. In the condensed phase, these chains could be dynamically cross-linked by adding a suitable cross-linking agent to generate a dynamic elastomer. The fact that the DA adducts linking the monomers can easily revert at room temperature even in the condensed phase accounts for the ability of the network to adapt in response to mechanical elongation stress or to self-repair, even after the system has reached its equilibrium. These findings extend to the molecular/covalent domain those properties displayed by supramolecular/non-covalent entities.[1,2,12] Fine-tuning the equilibrium constant of the connections used to form the dynamers should permit us to control the self-healing properties or to adapt the temperature range of the self-healing process.

Experimental Section

General: All reagents were purchased from commercial suppliers (Acros, Aldrich and Flucka) and used without further purification. Tetrahydrofuran (THF) was dried over sodium·benzophenone. Preparative adsorption flash column chromatography was performed by using silica gel (Geduran, silica gel 60 (230–400 mesh, 40–63 μm, Merck). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by using a Bruker Advance 400 spectrometer. The spectra were internally referenced to the residual solvent signal. In the assignments, the chemical shifts are given in ppm. The coupling constants J are listed in Hz. The following notation is used for the splitting patterns: singlet (s), doublet (d), triplet (t), q (quadruplet), multiplet (m). Electron impact (EI*)* mass spectra were performed by the Service de Spectrométrie de Masse, Institut de Chimie, Université Louis Pasteur. Electrospray (ESI and ESI-TOF) studies were performed by using a Bruker Micro TOF mass spectrometer. Sample solutions were introduced into the mass spectrometer source by using a syringe pump with a flow rate of 40 μL min^{-1}. Melting points were recorded by using a Büchi Melting Point B-540 apparatus and are uncorrected. Microanalyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur. SANS experiments were carried out by using the Pace spectrometer in the Léon Brillouin Laboratory at Saclay (LLB, France). The chosen incident wavelength, λ, depends on the set of experiments, as follows. For a given wavelength, the range of the amplitude of the transfer wave vector q was selected by changing the detector distance, D. Three sets of sample-to-detector distances and wavelengths were chosen ($D = 1$ m, $\lambda = 4.5 \pm 0.5$ Å; $D = 1.86$ m, $\lambda = 6 \pm 0.5$ Å; and $D = 4.7$ m, $\lambda = 12 \pm 1$ Å) so that the following q ranges were available : $4.2\times10^{-2} \leq q$ [Å^{-1}] $\leq 4.3\times10^{-1}$, $1.7\times10^{-2} \leq q$ [Å^{-1}] $\leq 1.8\times10^{-1}$ and $3.4\times10^{-3} \leq q$ [Å^{-1}] $\leq 3.4\times10^{-2}$, respectively. Measured intensities were calibrated to absolute values (cm^{-1}) by normalisation using the attenuated direct beam classical method. Standard procedures to correct the data for the transmission, detector efficiency and backgrounds (solvent, empty cell, electronic and neutronic background) were carried out. The scattered wave vector, q, is defined by Equation (5), in which θ is the scattering angle:

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{5}$$

The usual equation for absolute neutron scattering combines the intraparticle scattering $S_1(q) = V_{\text{chain}}\phi_{\text{vol}}P(q)$ form factor with the inter-particle scattering $S_2(q)$ factor:

$$I(q)(\text{cm}^{-1}) = (\Delta\rho)^2(S_1(q) + S_2(q)) = (\Delta\rho)^2(V_{chain}\phi_{\text{vol}}P(q) + S_2(q)) \tag{6}$$

in which $(\Delta\rho)^2 = (\rho_{\text{monomer}} - \rho_{\text{solvent}})^2$ is the difference per unit volume between the polymer and the solvent and was determined from the known chemical composition. $\rho = \Sigma n_i b_i/(\Sigma n_i m_i v \times 1.66\times10^{-24})$ represents the scattering length per unit volume, b_i is the neutron scattering length of species i, m_i is the mass of species i and v is the specific volume of the monomer (which has been taken to be equal to 0.89 cm^{3}g^{-1}) or the solvent (e.g., 1.1494 cm^{3}g^{-1} for deuterated acetone). $P(q)$ is the form factor, $V_{\text{chain}} = Nvm \times 1.66\times10^{-24}$ is the volume of N monomers (of mass m) in a chain and ϕ_{vol} is the volume fraction of monomer. At high q ranges, the scattering is assumed to arise from isolated chains, that is, $S_2(q) = 0$, and thus $I(q) \propto P(q)$.

2,3-Dicyano-but-2-enedioic acid 2-(2,3-dicyano-3-methoxycarbonyl-acryloyloxy)-ethyl ester methyl ester (2): Ethylene glycol dicyanoacetate (2.0 g, 10.2 mmol) and methylcyanoacetate (4.5 mL, 5 equiv) were dissolved in dry tetrahydrofuran (20 mL). Thionyl chloride (6.0 mL, 9.7 g, 8 equiv) was added, and the mixture was heated at reflux overnight under an inert atmosphere. The reaction mixture was then cooled to RT, and the precipitate that formed was filtered. This solid was suspended in chloroform, filtered again, washed with ethyl acetate/chloroform (2:1) and dried under reduced pressure to give the product as a white solid (1.83 g, 46 %). M.p. >180 °C decomp; ^{1}H NMR ([D$_6$]DMSO, 400 MHz): $\delta = 4.67$ (s, 4 H), 3.93 ppm (s, 6 H); ^{13}C NMR ([D$_6$]DMSO, 100 MHz): $\delta =$ 158.7, 158.1 (−*C*(=O)O−), 125.7, 125.0 (*C*=*C*), 112.6, 112.4 (−*C*≡N), 65.2 (O−*C*−*C*−O), 55.0 ppm (O−*C*); ESI-TOF-MS: *m*/*z* (%): calcd for $C_{16}H_{10}N_4O_8Na^+$: 409.0391 [*M*+Na]$^+$; found: 409.0447 (100); elemental analysis calcd (%) for $C_{16}H_{10}N_4O_8$: C 49.75, H 2.61, N 14.50; found: C 48.46, H 2.97, N 16.99.

General procedure for the synthesis of solid tricyanoethylenecarboxylates: TCNE (6.0 g, 5.5 equiv) was dissolved in dry tetrahydrofuran (30 mL) at 70 °C. Cyanoacetate (8.5 mmol) was added, followed by pyridine (100 μL), which caused the reaction mixture to become dark. The mixture was refluxed for 40 h, then allowed to cool down to RT and then diluted with chloroform (50 mL) and pentane (100 mL). The mixture was allowed to stand for 1 h, during which a black tarry phase settled out and some of the excess TCNE precipitated. The precipitate was filtered off and the filtrate was washed repeatedly with water until the organic layer became a light red/purple colour. It was then dried over magnesium sulphate and concentrated under reduced pressure until a precipitate started to form. The mixture was filtered, then heptane (50 mL) was added to the filtrate and the solution concentrated again. When a precipitate started to form, the solution was cooled to 0 °C and the white solid that formed was filtered off. If necessary, this solid was recrystallised from a mixture of chloroform (10 %) in pentane. This operation was repeated until the ^{13}C NMR spectrum showed no trace of TCNE.

*Methyl tricyanoethylenecarboxylate (**3**)*: The product was obtained as a white powder (4 %). M.p. 89–91 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta =$ 4.11 ppm (s, 3 H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 156.4$. (−*C*(=O)O−), 131.3 (C=*C*(−CN)−C(=O)−), 110.6, 109.4, 108.3 (3×−*C*≡N), 106.6 (C=*C*(−CN)$_2$), 55.6 ppm (O−*C*); elemental analysis calcd (%)for $C_7H_3N_3O_2$: C 52.18, H 1.88, N 26.08; found: C 52.48, H 1.73, N 25.94.

*Ethyl tricyanoethylenecarboxylate (**4**)*: The product was obtained as a white powder (14 %). M.p. 65–66 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta =$ 4.55 (q, ^3J(H,H) = 7.1 Hz, 2 H), 1.49 ppm (t, ^3J(H,H) = 7.1 Hz, 3 H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 155.8$. (−*C*(=O)O−), 131.9 (C=*C*(−CN)−C(=O)−), 110.7, 109.4, 108.4 (3×−*C*≡N), 106.4 (C=*C*(−CN)$_2$), 66.0 (O−*C*−C), 13.8 ppm (O−C−*C*); EI-MS: *m*/*z*: calcd for $C_{16}H_4N_6O_4Na^+$: 175.04 [*M*]$^+$; found: 175.0; elemental analysis calcd (%) for $C_8H_5N_3O_2$: C 54.86, H 2.88, N 23.99; found: C 54.59, H 2.97, N 24.72.

*Allyl tricyanoethylenecarboxylate (**5**)*: The product was obtained as a white powder that must be stored at −30 °C (26 %). M.p. >117 °C decomp; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 6.01$ (ddt, ^3J(H,H) = 17.2, 10.2, 6.4 Hz, 1 H), 5.58 (dd, ^3J(H,H) = 17.2, ^4J(H,H) = 1.2 Hz, 1 H), 5.52 (dd, ^3J(H,H) = 10.2, ^4J(H,H) = 0.6 Hz, 1 H), 4.98 ppm (ddd, ^3J(H,H) = 6.4, ^4J(H,H) = 1.2, 0.6 Hz, 2 H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 155.7$ (−*C*(=O)O−), 131.7 (C=*C*(−CN)−C(=O)−), 128.9 (C−*C*=C), 122.3 (C−C=*C*), 110.7, 109.5, 108.4 (3×−*C*≡N), 105.5 (C=*C*(−CN)$_2$), 90.1 (O−*C*(−C)$_3$), 27.6 ppm (O−C−*C*); elemental analysis calcd (%) for $C_9H_5N_3O_2$: C 57.76, H 2.69; found: C 57.71, H 2.96 (N was not determined).

tert-*Butyl tricyanoethylenecarboxylate (**6**)*: The product was obtained as a white powder that must be stored at −30 °C (41 %). M.p. 102–103 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 1.65$ ppm (s, 9 H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 154.5$ (−*C*(=O)O−), 133.8 (C=*C*(−CN)−C(=O)−), 111.0, 109.6, 108.6 (3× −*C*≡N), 106.6 (C=*C*(−CN)$_2$), 69.9 (O−*C*=C), 27.6 (O−C−*C*);. EI-MS: *m*/*z* calcd for $C_6N_3O^+$: 130.01 [*M*−O*t*Bu]$^+$; found: 130.1; elemental analysis calcd (%) for $C_{10}H_9N_3O_2$: C 59.11, H 4.46, N 20.68; found: C 59.10, H 4.03, N 22.15.

Ester 1: The pure compound was obtained from the first crystallisation as a white solid (12%). M.p. >152°C decomp; ^{1}H NMR ([D$_6$]acetone, 400 MHz): $\delta = 5.24$ ppm (s, 4H); ^{13}C NMR ([D$_6$]acetone, 100 MHz): $\delta =$ 156.0 (−*C*(=O)O−), 131.6 (C=*C*(−CN)−C(=O)−), 111.6, 110.6, 109.1 (3× −*C*≡N), 106.8 (C=*C*(−CN)$_2$), 80.8 (O−C−*C*≡), 55.2 ppm (O−*C*−C≡); ESI-TOF-MS: *m*/*z* (%): calcd for $C_{16}H_4N_6O_4Na^+$: 367.0186 [*M*+Na]$^+$; found: 367.0219 (100).

4-(Cyclopenta-2,4-dien-1-ylidene)pentanoic acid (7): Levulinic acid (4.0 g, 35 mmol) was dissolved in tetrahydrofuran (45 mL) and methanol (5 mL) at 0°C. Freshly distilled cyclopentadiene (7.3 mL, 5.9 g, 2.5 equiv) and pyrrolidine (5.8 mL, 4.5 g, 2 equiv) were added. After 30 min at 0°C, the reaction mixture was allowed to warm to RT, then left to react for another 3 h. The reaction mixture was then poured into diethyl ether (100 mL) and washed with a 0.1 M aqueous solution of hydrochloric acid. The diethyl ether layer was then extracted twice with an aqueous solution of sodium hydroxide (0.1 M, 100 mL). The two basic aqueous phases were combined, poured into dichloromethane (200 mL) and acidified to pH 2 with concentrated hydrochloric acid. The phases were separated and the aqueous layer was extracted twice more with dichloromethane. The combined organic phases were dried over magnesium sulphate and evaporated to dryness under vacuum. The residual yellow oil was purified by using chromatography on silica gel with ethyl acetate as the eluent to give **7** as a yellow solid (71%). M.p. 66–67°C; ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 11.85$ (br s, 1H), 6.54 (m, 4H), 2.91 (t, $J = 7.3$ Hz, 2H), 2.64 (t, $J = 7.3$ Hz, 2H), 2.25 ppm (s, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 172.4$ (−*C*(=O)OH), 150.2 (C=*C*−(C=C)$_2$), 143.3 (*C*=C−(C=C)$_2$), 131.4, 131.2 (C=*C*−*C*=C), 120.7, 120.3 (*C*=C−C=*C*), 33.4, 31.5 (*C*−C(=O)OH + C−*C*−C=), 20.6 ppm (*C*−C=); ESI-TOF-MS: *m*/*z* calcd for $C_{10}H_{13}O_2^+$: 165.0910 [*M*+H]$^+$; found: 165.0892 (100%); elemental analysis calcd (%) for $C_{10}H_{12}O_2$: C 73.15, H 7.37; found: C 73.27, H 7.43.

Polyethylene glycol bis(fulvene) (8): Acid **7** (4.1 g, 5 equiv) and DCC (5.2 g, 5 equiv) were dissolved in dichloromethane (100 mL) with DMAP (5 mg). Precipitation occurred and PEG 400 (2.0 mL, 6.8 mmol) was added. The reaction was carried out at RT for two days. The precipitate was filtered, then the filtrate was evaporated to dryness under reduced pressure. Chromatography on silica gel with a gradient of ethyl acetate and an increasing amount of methanol (up to 5%) as the eluent gave **8** as a viscous yellow oil ($M_r \approx 680$, 1.21 g, 35%). ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 6.50$ (m, 8H), 4.24 (t, ^3J(H,H) = 4.9 Hz, 4H), 3.69 (t, ^3J(H,H) = 4.9 Hz, 4H), 3.65–3.67 (m, ≈25H), 2.88 (t, ^3J(H,H) = 7.9 Hz, 4H), 2.60 (t, ^3J(H,H) = 7.9 Hz, 4H), 2.22 ppm (s, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 172.4$ (−*C*(=O)O−C), 150.2 (C=*C*−(C=C)$_2$), 143.4 (*C*=C−(C=C)$_2$), 131.4, 131.2 (C=*C*−*C*=C), 120.7, 120.3 (*C*=C−C=*C*), 70.6 (−C−O−*C*−*C*−O−C−), 69.0 (C(=O)−O−C−*C*−O−), 63.8 (C(=O)−O−*C*−), 33.5, 31.8 (*C*−C(=O)O−C + C−*C*−C=), 20.6 ppm (*C*−C=); ESI-TOF-MS: *m*/*z* calcd for $C_{36}H_{54}O_{11}Na^+$ (i.e., 8 ethylene glycols): 685.3558 [*M*+Na]$^+$; found: 685.3499 (100%).

Pentaerythritol ethoxylate tetra(fulvene) (10): Acid **7** (2.7 g, 5.5 equiv) and DCC (3.4 g, 5.5 equiv) were dissolved in dichloromethane (100 mL) with DMAP (5 mg). Precipitation occurred and pentaerythritol ethoxylate (2.0 mL, 3.0 mmol, $M_n = 797$, $n = i+j+k+l \approx 15.0$; see Scheme 5) was added. The reaction was carried out at RT for two days. The precipitate was filtered, then the filtrate was evaporated to dryness under reduced pressure. Chromatography on silica gel with a gradient of ethyl acetate and an increasing amount of methanol (up to 5%) as the eluent gave **10** as a viscous yellow oil ($M_r \approx 1290$ g mol^{-1}, 2.16 g, 56%, $n = i+j+k+l \approx 13$; see Scheme 5). ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta = 6.50$ (m, 16H), 4.23 (t, ^3J(H,H) = 4.7 Hz, 8H), 3.50–3.75 (m, ≈98H), 3.45 (br s, 8H), 2.87 (t, ^3J(H,H) = 7.6 Hz, 8H), 2.60 (t, ^3J(H,H) = 7.6 Hz, 8H), 2.21 ppm (s, 12H); ^{13}C NMR (CDCl$_3$, 100 MHz): $\delta = 172.4$ (−*C*(=O)O−C), 150.2 (C=*C*−(C=C)$_2$), 143.3 (*C*=C−(C=C)$_2$), 131.4, 131.2 (C=*C*−*C*=C), 120.7, 120.3 (*C*=C−C=*C*), 71.0, 70.9, 70.6, 70.3, 69.0, 63.8, 53.4 (*C*−O), 44.5 (*C*−C$_4$), 33.5, 31.8 (*C*−C(=O)O−C + C−*C*−C=), 20.5 (*C*−C=).

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