Soft-to-hard transformation of the mechanical properties of dynamic covalent polymers through component incorporation†

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The mechanical properties of acylhydrazone dynamic polymers may be converted from soft to hard by the incorporation of rigid monomeric components into the original soft polymer backbone, taking advantage of acylhydrazone bond exchange.

Dynamic polymers, dynamers,[1,2] are polymeric entities of either molecular or supramolecular nature that are capable of undergoing exchange, incorporation or decorporation of their monomeric subunits, linked together by respectively reversible covalent bonds or labile non-covalent interactions. Dynamers implement constitutional dynamic chemistry,[1,3] the chemistry of molecular and supramolecular entities capable of dynamically modifying their constitution by exchanging/incorporating molecular components.

On the molecular level, dynamic covalent chemistry[1,3–7] has recently attracted considerable attention as a powerful methodology for discovering biologically active substances,[5,7] as well as for developing new functional materials[3,5,8] such as dynamic covalent polymers.[1,8–13] In addition to conventional polymeric properties such as stability and strength, these dynamic polymers present the distinctive ability to exchange, incorporate and/or decorporate monomeric components linked by reversible covalent bonds, for example acylhydrazone functions,[6,7,10,11,14] alkoxyamine units[12] or imine metathesis,[13] depending on the external conditions. This feature offers to polymer science perspectives towards a functional plasticity that involves modification and control of the intrinsic properties of polymeric entities from within.[1,10–12] Because the mechanical behavior of polymers plays a most important role in materials science, the ability to mutate the mechanical properties of polymers would be of much interest, giving access to a new class of functional polymeric materials. We now report that dynamic covalent polymers based on an acylhydrazone backbone can undergo a progressive change in their mechanical properties through the introduction of other monomeric components into their main chain.

The bis-hydrazide monomers **M1** and **M2** were formed by treatment of the corresponding methyl or ethylesters with hydrazine monohydrate in alcohol. The dialdehydes **M3** and **M4** were obtained, respectively, from 4-allyloxybenzaldehyde and hexamethyltrisiloxane using Karstedt catalyst, and from 4-hydroxy-2-methoxybenzaldehyde and 2-chloroethylether in presence of K_2CO_3 (Fig. 1).

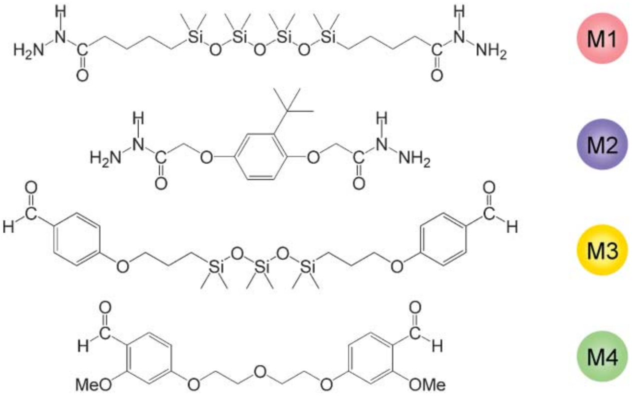

Fig. 1 Structures of the bis-hydrazides **M1** and **M2**, and of the dialdehydes **M3** and **M4**.

Polycondensation‡ in $CHCl_3$ between the monomers **M1** and **M3**, both containing a highly flexible siloxane-derived spacer unit as *soft* components, yielded the alternating homopolymer **P1** as a very soft and quite stretchy film **F1** (of about 0.057 mm thickness) after solvent evaporation (Fig. 2). Gel permeation chromatography (GPC) gave a molecular weight M_n = 41 000 and a distribution M_w/M_n = 1.6 (with polystyrene calibration). Differential scanning calorimetry (DSC) yielded a glass transition temperature T_g = 1 °C, respectively. Viscoelasticity measurements revealed that the storage elastic modulus E' of **F1** was 0.015 GPa at 25 °C, indicating that it possessed rubber elasticity at room temperature (Fig. 3). The profile of the loss elastic modulus, E'', gave T_g = 10 °C. These results are in line with the soft and stretchy behavior of **F1**, as shown in Fig. 2. The small decrease of E' between −80 °C and −40 °C must arise from the siloxane units of the polymer **P1**.

On the other hand, polycondensation between the monomers **M2** and **M4**, containing rigid spacer groups as *hard* components, gave the alternating homopolymer **P2** as a hard but very fragile film **F2** with M_n = 14 000, M_w/M_n = 1.8 and T_g = 100 °C (determined by GPC and DSC, respectively). It was impossible to

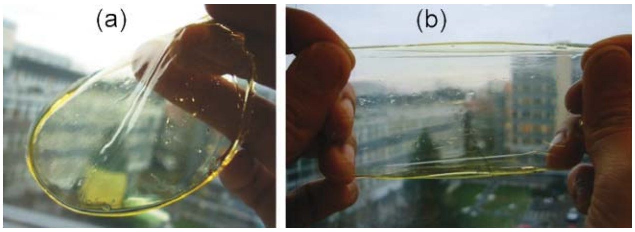

Fig. 2 The soft and stretchy polymer film **F1**.

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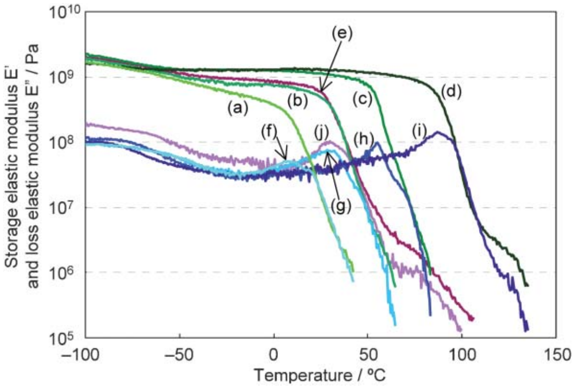

Fig. 3 Temperature dependence of the storage elastic modulus E' of the films (a) **F1**, (b) **F8**, (c) **F6**, (d) **F7** and (e) **F9**, and the loss elastic modulus E'' of the films (f) **F1**, (g) **F8**, (h) **F6**, (i) **F7**, and (j) **F9**.

further study the mechanical properties of **F2** as it was not strong enough for such experiments.

The homopolymers **P3** and **P4**, and the random copolymer **P5** were also prepared as reference materials, respectively, from monomers **M1** and **M4**, **M2** and **M3**, and all four kinds of monomer in equal molar ratio in the same manner. ^{1}H NMR analyses in 1 : 1 DMSO-d_6/CD$_2$Cl$_2$ solution (*ca.* 8 mg ml^{-1}) allowed identification of the four different connections between hydrazides and aldehydes by the signals of the N=C–H protons of the acylhydrazone functions between 7.8–8.7 ppm (Fig. 4).

Changes to the mechanical properties of acylhydrazone polymers induced by bond interchange and component incorporation was demonstrated by introducing hard components, that is **M2** and **M4**, into the soft homopolymer structure **P1**. Equimolar amounts of **P1**, on the basis of its repeating unit, **M2** and **M4** were dissolved in CHCl$_3$ in the presence of acid, followed by heating the solution to accelerate the exchange reaction. Solvent evaporation then gave the transparent film **F6**.§ The film **F6** was distinctly harder than the parent film **F1**, quite enough to stand by itself (Fig. 5). The ^{1}H NMR spectrum of **F6** (in 1 : 1 DMSO-d_6/CD$_2$Cl$_2$) showed that there were four kinds of signals of nearly equal area, which were assigned to the C–H protons of the acylhydrazone connections between **M1** and **M3**, **M1** and **M4**, **M2** and **M3**, and **M2** and **M4** (Fig. 6). This observation indicated that monomers **M2** and **M4** were introduced into the main chain of the homopolymer **P1**, generating a random copolymer **P6**, obtained as the film **F6**, which should be similar to the random copolymer **P5**, obtained from the mixture of the four components **M1–M4**. GPC gave M_n = 59 000 and M_w/M_n = 1.5 (with polystyrene calibration) for **P6**, of the same order as the parent homopolymer **P1**. However, determining how random the sequences are is not possible from the NMR spectra.

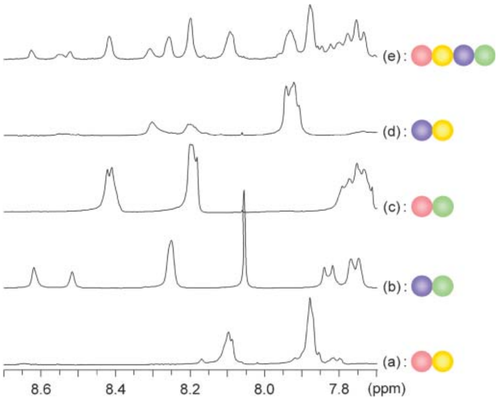

Fig. 4 Part of the ^{1}H NMR spectra of the homopolymers (a) **P1**, (b) **P2**, (c) **P3** and (d) **P4**, and (e) the random copolymer **P5** in a 1 : 1 mixture of DMSO-d_6/CD$_2$Cl$_2$ (*ca.* 8 mg ml^{-1}) showing the C–H proton signals of the acylhydrazone functions (signal of CHCl$_3$ remaining in the polymers is at around 8.1 ppm).

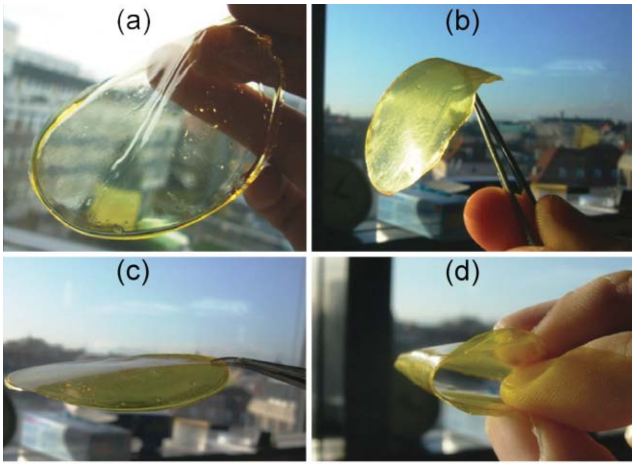

Fig. 5 Evolution in appearance of the mechanical properties of the polymer films (a) **F1**, (b) **F8**, (c) **F6** and (d) **F7**.

Introduction of **M2** and **M4** into homopolymer **P1** led to a striking evolution in its mechanical properties. The glass transition temperature, T_g, of **P6** increased to 56 °C, beyond room temperature, compared to 10 °C for **P1** (based on the loss elastic modulus E''). This increment nicely reflected the difference in film hardness at room temperature between **F1** and **F6**, illustrated in Fig. 5. The E' profile of **F6** indicated that it had a typical glass state up to around 50 °C and rubber elasticity around 70 °C.

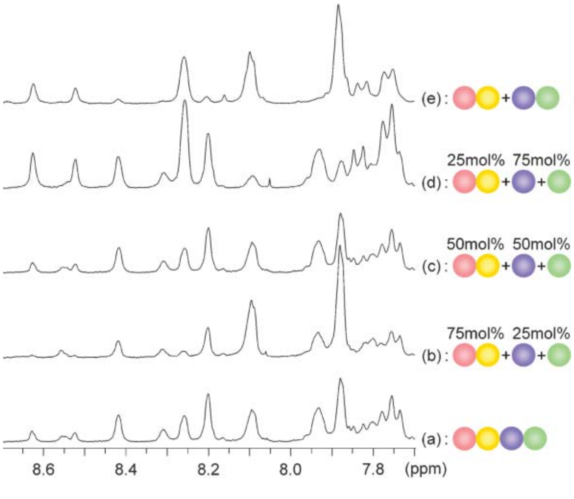

Fig. 6 Part of the ^{1}H NMR spectra of (a) the random copolymer **P5**, the modified polymers (b) **P8**, (c) **P6** and (d) **P7**, and (e) the polymer blend **P9** in a 1 : 1 mixture of DMSO-d_6/CD$_2$Cl$_2$ (*ca.* 8 mg ml^{-1}) showing the C–H proton signals of the acylhydrazone functions (the signal of CHCl$_3$ remaining in the polymers at around 8.1 ppm).

Table 1 Evolution in mechanical properties of the dynamic acylhydrazone polymer films **F1–F7** as a function of the incorporation of monomers **M2** and **M4** into polymer **P1**[a]

Film	Ratio of **M2** and **M4** to **P1** (mol%)[b]	Thickness/mm	M_n[c]	M_w/M_n[c]	T_g (DSC)/°C[d]	T_g (E'')/°C[e]	E'/GPa[f]
F1	0	0.057	41 000	1.6	1	10	0.015
F2	100	—[g]	14 000	1.8	100	—[g]	—[g]
F8	25	0.049	47 000	1.5	—[g]	32	0.48
F6	50	0.049	59 000	1.5	46	56	1.1
F7	75	0.055	75 000	1.5	—[g]	88	1.3
F9	50	0.039	34 000	2.1	19	30	0.59

[a] In presence of 2.5 mol% acid per acylhydrazone unit for **F6–F8**; no acid added for **F9**. [b] Total molar ratio of **M2** and **M4** in the resulting polymers on the basis of monomer units. [c] Molecular weight M_n and distribution M_w/M_n determined by GPC with polystyrene calibration. [d] Glass transition temperature determined by DSC. [e] Glass transition temperature determined by the profile of the loss elastic modulus E''. [f] Storage elastic modulus E' at 25 °C. [g] Not determined.

The degree of evolution in mechanical properties was correlated with the ratio of **M2** and **M4** incorporated into the resulting polymers (Table 1). Three molar equivalents of **M2** and **M4**, on the basis of **P1** units, led to a film **F7** (harder than **F6**), whereas one third of both **M2** and **M4** gave film **F8** (softer than **F6**) (Fig. 5). The ^{1}H NMR spectra of **F7** and **F8** showed that both were also random copolymers **P7** and **P8**, respectively, consisting of **M1**, **M2**, **M3** and **M4** in approximately the expected ratios. In the case of **P7**, for instance, the ratio of the peak areas assigned to the connections between **M1** and **M3**, **M1** and **M4**, **M2** and **M3**, and **M2** and **M4** was about 1 : 3 : 3 : 9, whereas **P7** was a random copolymer made of **M1**, **M2**, **M3** and **M4** in about a 1 : 3 : 1 : 3 molar ratio, as expected. T_g and viscoelasticity values were in accordance with the proportion of **M2** and **M4** in the polymers. The mechanical properties of these resulting polymers were thus markedly different from those of the parent homopolymer **P1** or **P2**, implying that the mechanical properties of the acylhydrazone polymers are adjustable *via* the nature and/or the proportion of the different components incorporated.

In contrast, lack of incorporation did not bring evolution in mechanical properties, leading only to the behavior expected for a blend of the parent polymers **P1** and **P2**. Thus, a slightly cloudy film, **F9**, was obtained from an equimolar ratio mixture of **P1** and **P2** heated in $CHCl_3$ solution for 24 h in the *absence* of acid, followed by solvent evaporation. The ^{1}H NMR spectrum of **F9** showed that it was just a polymer blend, **P9**, of **P1** and **P2** with only a very small amount of exchange (<5%). The film **F9** seemed to be softer than **F6**, although both **F9** and **F6** consisted originally of the same segments. Single glass transition temperatures for **P9** were observed based on both DSC and the loss elastic modulus E'', respectively, and were about 20 °C higher than those of **P1**. The profile of the storage elastic modulus, E', showed that **P9** possessed a glass state up to around 30 °C, and that E' itself decreased with relative moderation above T_g as the temperature increased. These observations implied that **P2** was microdispersed in a **P1** matrix at a nanometer scale in the polymer blend **P9**.

In conclusion, the present results show that the mechanical properties of polyacylhydrazone dynamers can be varied through incorporation of other components into the main chain of the original polymer, making use of the reversible nature of the acylhydrazone bond. This feature provides a very useful methodology for modifying the mechanical properties of polymers, giving access to smart and adaptive dynamic materials[1,8] such as self-strengthening polymeric materials controlled-by and responding-to external stimuli. Such behavior by dynamers is thus a result of the application of the principles of constitutional dynamic chemistry[1,3] to polymer science.

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Notes and references

‡ The bis-hydrazide(s) and dialdehyde(s) at concentrations of around 0.1 M were each dissolved in a 1 : 1 stoichiometry in $CHCl_3$ and heated to 60 °C for 3 h. The solution was poured into a 50 mm diameter Petri dish made of fluoroplastic, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared, and then kept at 60 °C *in vacuo* for 24 h. About 200 mg of the total amounts of the monomers were used to obtain the polymer film of around 0.04–0.06 mm thickness. The films thus obtained were used as such for the study of their mechanical properties and usually contained trace amounts of $CHCl_3$, as determined by ^{1}H NMR.

§ Equimolar amounts of polymer **P1**, on the basis of its repeating unit, bis-hydrazide **M2** and dialdehyde **M4** were dissolved in $CHCl_3$ (the concentration was around 0.05 M), followed by the addition of pentadecafluorooctanoic acid in 0.025 molar ratio with respect to the resulting total acylhydrazone bonds. The solution was heated to 60 °C for 24 h and then poured into a Petri dish, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared, and then *in vacuo* for 24 h at the same temperature.

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