Dynamic polymer blends—component recombination between neat dynamic covalent polymers at room temperature

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Dynamic polymers based on acylhydrazone bonds in the linear main chains were found to show bond exchange leading to crossover component recombination as neat polymers even at room temperature under acid catalysis, thus generating randomized copolymers.

Dynamic covalent chemistry is based on reversible covalent bonds, whose formation and dissociation can be controlled through the physical and chemical conditions of the environment.[1–4] It offers the possibility to develop methodologies toward new functional materials such as dynamic covalent polymers[1–10] and dynamers.[6] Among the known reversible covalent bonds, the acylhydrazone functionality, resulting from the condensation of hydrazides with carbonyl groups, is particularly promising in view of its thermodynamic stability, the facile control of its reversibility and the wide structural variability of its components.[6,11–13] Although most of the reversible reactions have been performed either in solution and/or under heating,[6–13] it would be of much interest, especially to materials science, to be able to perform such reversible chemistry also in neat phase without heating. We now report that polyacylhydrazones are able to undergo recombination of their components as neat polymers at ordinary temperature with acid catalyst in the absence of external stimuli.

The bis-hydrazide monomers **M1** and **M2** were obtained by treatment of the corresponding methylesters with hydrazine monohydrate in methanol. The dialdehydes **M3** and **M4** were obtained from the corresponding hydroxybenzaldehydes and bis[2-(2-chloroethoxy)ethyl]ether (Fig. 1). Polycondensation† between the monomers **M1** and **M3**, **M2** and **M4**, **M1** and **M4**, and **M2** and **M3** gave respectively, the homopolymers, **P1**, **P2**, **P3** and **P4**, as transparent films after solvent evaporation (Fig. 2). The random copolymer **P5** was also prepared from the 4 kinds of monomers in equal molar ratio.

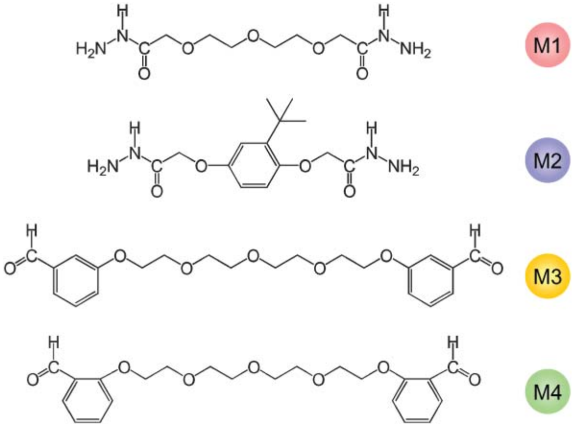

Fig. 1 Structures of the bis-hydrazides **M1** and **M2**, and the dialdehydes **M3** and **M4**.

The occurrence of bond exchange and crossover component recombination was demonstrated by the use of polymer blends. Two such blends were prepared‡ by just mixing two homopolymers **P1** and **P2** either in the presence (**B1**) or absence (**B2**) of added acid giving transparent films (of about 0.035 mm thickness) which were flexible and slightly sticky but hard enough to stand by themselves and be cut easily with scissors (Fig. 3). Gel permeation chromatography gave a molecular weight M_n = 35000 and a distribution M_w/M_n = 3.0 for the polymer blend **B2** (with polystyrene calibration). These polymer blends contained 2.1 wt% of water (determined by the Karl Fischer method) and 13 wt% of $CHCl_3$ (determined by ^1H NMR).

^1H NMR analyses in DMSO–d_6 (*ca.* 8 mg ml^{-1}) allowed identification of the connections between hydrazides and aldehydes by the signals of the C–H protons of the acylhydrazone functions between 7.8–8.7 ppm (Fig. 4). The spectrum of **B1** showed a weak signal (around 7.94 ppm) assigned to the connection between **M2** and **M3**, indicating that some crossover exchange had occurred during the preparation of the film of polymer blend (about 6% of the acylhydrazone bonds). On the other hand, in the absence of the acid, no exchange reaction was detected while the film was formed, the blend **B2** being just the simple mixture of **P1** and **P2**.

Exchange within the blend polymer was followed by observing the changes of the ^1H NMR spectrum of **B1**. The acid containing polymer blend **B1** was stored neat at 23–25 °C in small sealed tubes wrapped in aluminium foil to avoid exposure to light. It was dissolved in DMSO-d_6 within 5–10 min at room temperature without heating for spectroscopic studies. After storage for 3 days, the signal corresponding to the **M2/M3** connection had increased distinctly, indicating that about 32% acylhydrazone bond exchange had taken place within the neat blend. Although there was no specific change in appearance of the film, the ratio of exchanged

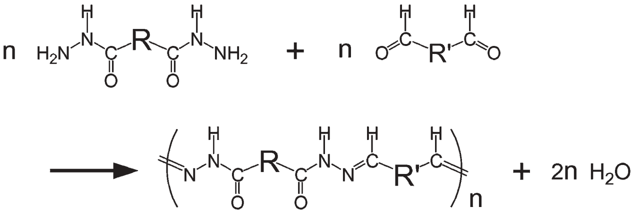

Fig. 2 Polycondensation of bis-hydrazides with dialdehydes forming polyacylhydrazones.

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Fig. 3 The polymer blend film **B1**.

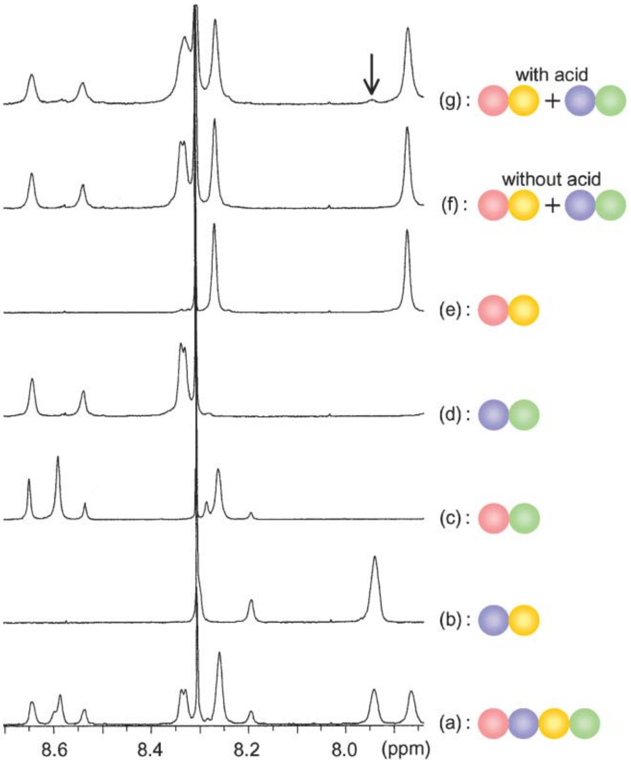

Fig. 4 Part of the ^{1}H NMR spectra of (a) the random copolymer **P5**, the homopolymers (b) **P4**, (c) **P3**, (d) **P2**, (e) **P1**, and the polymer blends (f) without acid **B2** and (g) with acid **B1** in DMSO-d$_6$ (*ca.* 8 mg ml^{-1}) showing the C–H proton signals of the acylhydrazone functions (signal of CHCl$_3$ remaining in the polymers at around 8.32 ppm).

acylhydrazone bond rose to 57% and 82% when kept under the same conditions for 10 days and for 30 days, respectively (Fig. 5). No signal assigned to monomers was observed in the ^{1}H NMR spectra. The spectra of polymer blend **B1** evolved toward that of the random copolymer as time went by. Furthermore, only slight exchange was observed when the neat polymer blend **B1** was kept at 8 °C or −30 °C, even after 10 days (about 7% in both cases).

Although the exchange reactions occurred at ambient temperature in the absence of external stimuli, they were enhanced by heating (Table 1). Heating the neat polymer blend **B1** at 80 °C for 10 min led to 58% exchange, and after 10 min at 120 °C almost complete exchange had occurred, generating a compound which should be fairly the same as a random copolymer **P5**.

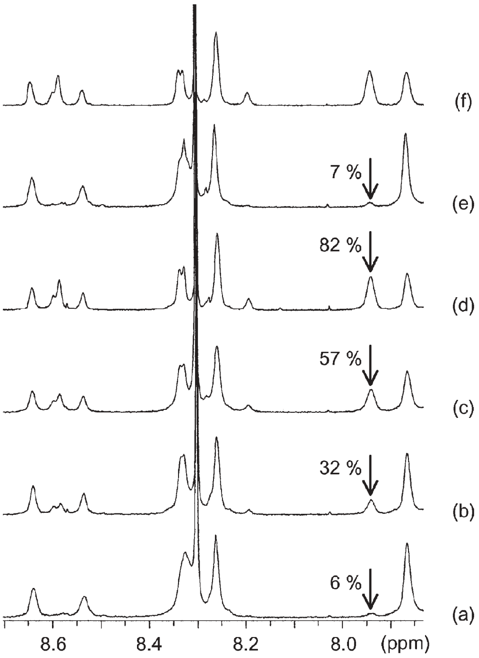

Fig. 5 Part of the ^{1}H NMR spectra of (a) the polymer blend **B1**, stored at 23–25 °C for (b) 3 days, (c) 10 days, (d) 30 days, (e) at −30 °C for 10 days and (f) the random copolymer **P5** (signal of CHCl$_3$ remaining in the polymers at around 8.32 ppm).

Table 1 Effect of heating on the exchange reactions in the neat polymer blend **B1**

	2 min	10 min
120 °C	87%	99%
100 °C	53%	84%
80 °C	36%	58%

The acid catalyst is indispensable for significant exchange to occur. In its absence, there was only 2% and 5% exchange on heating the neat polymer blend **B2** at 100 °C and 120 °C for 4 h, respectively. If stored at room temperature, no trace of reaction was observed even after 30 days.

Exchange proceeds much less efficiently in solution than in the neat polymer blend. When **B1** was dissolved in DMSO–d$_6$ (*ca.* 8 mg ml^{-1}) and the solution stored at 23–25 °C, there was only 8% and 11% exchange after, respectively, 10 days and 30 days (on the basis of an initial value 6%). This dramatic decrease may be related to an insufficient quantity of acid for exchange in solution phase. The molar ratio of acid to total acylhydrazone groups (0.01 equivalent) is indeed much lower than commonly used for the dynamic combinatorial libraries (for example, one equivalent of a perfluoroacid was used to reach equilibrium in two days[11c]). Thus, the acid acts as catalyst much more effectively in neat phase than in solution.

The present results show that acylhydrazone dynamers are capable of interchanging their bonds mutually as neat polymers even at room temperature in the absence of external stimuli, inducing crossover between polymeric chains (Fig. 6). Such polymers have promising potential as smart, adaptive materials, namely self-repairing or self-strengthening (through chain crossover) materials. These features provide access to useful methods for reorganization, modification or hybridisation of polymers without solvents. They illustrate the potential offered by the

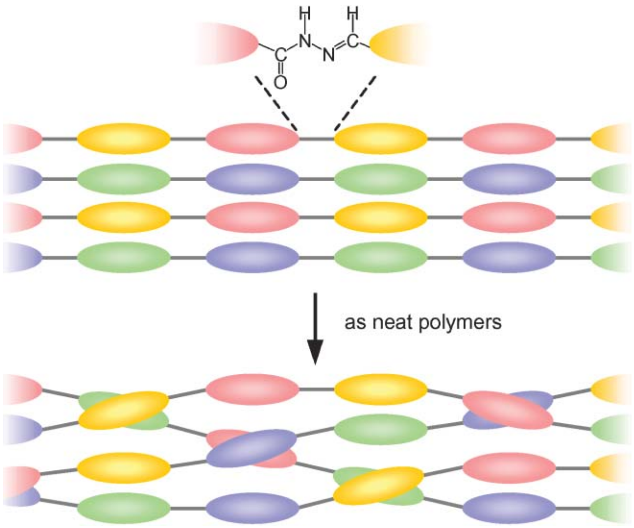

Fig. 6 Schematic representation of crossover component recombination by dynamic bond rearrangement in polyacylhydrazone dynamers.

application of the principles of constitutional dynamic chemistry[4,6] to materials science.

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Notes and references

† The bis-hydrazide(s) and the dialdehyde(s) were dissolved in 1:1 stoichiometry in $CHCl_3$ and heated to 60 °C for 2 h. The concentrations were around 0.1–0.3 M depending on the solubilities of the monomers. The solution was poured into a petri dish made of fluoroplastic followed by evaporation *in vacuo* at 23–25 °C until most of the solvent had disappeared and then heating to 60 °C for 1 h at normal pressure with slight Ar flow.

‡ Polymers **P1** and **P2** were dissolved in a $CHCl_3$ in 1:1 molar ratio (the total concentrations were around 40–60 mg cc^{-1}), followed by addition of $CHCl_3$ solution of pentadecafluorooctanoic acid (*ca.* 4 mM), molar ratio 0.01 with respect to the total acylhydrazone bonds in the polymers. The solution was immediately mixed and poured into a petri dish, then evaporated *in vacuo* (8 mmbar) at 23–25 °C for 18 h (**B1**). The polymer blend without the acid was also prepared in the same way (**B2**). A small ^1H NMR signal assigned to **M3**, corresponding to *ca.* 1 molar %, was observed in the case of **B2**.

1 S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2002, **41**, 898.
2 J.-M. Lehn, *Chem. Eur. J.*, 1999, **5**, 2455.
3 J.-M. Lehn, in *Supramolecular Science: Where It Is and Where It Is Going*, Eds.: R. Ungaro and E. Dalcanale, Kluwer, Dordrecht, The Netherlands, 1999, p. 287.
4 J.-M. Lehn, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4763; J.-M. Lehn, *Science*, 2002, **295**, 2400.
5 J.-M. Lehn, *Polym. Int.*, 2002, **51**, 825.
6 W. G. Skene and J.-M. Lehn, *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 8270.
7 X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698.
8 H. Otsuka, K. Aotani, Y. Higaki and A. Takahara, *Chem. Commun.*, 2002, 2838; H. Otsuka, K. Aotani, Y. Higaki and A. Takahara, *J. Am. Chem. Soc.*, 2003, **125**, 4064.
9 T. Nishinaga, A. Tanatani, K. Oh and J. S. Moore, *J. Am. Chem. Soc.*, 2002, **124**, 5934.
10 N. Giuseppone and J.-M. Lehn, *J. Am. Chem. Soc.*, 2004, **126**, 11448.
11 (*a*) G. R. L. Cousins, S.-A. Poulsen and J. K. M. Sanders, *Chem. Commun.*, 1999, 1575; (*b*) G. R. L. Cousins, S.-A. Poulsen and J. K. M. Sanders, *Curr. Opin. Chem. Biol.*, 2000, **4**, 270; (*c*) G. R. L. Cousins, R. L. E. Furlan, Y.-F. Ng, J. E. Redman and J. K. M. Sanders, *Angew. Chem. Int. Ed.*, 2001, **40**, 423.
12 R. Nguyen and I. Huc, *Chem. Commun.*, 2003, 942.
13 O. Ramström and J.-M. Lehn, *Nature Reviews, Drug Discovery*, 2001, **1**, 26; O. Ramström, S. Lohmann, T. Bunyapaiboonsri and J.-M. Lehn, *Chem. Eur. J.*, 2004, **10**, 1711; S. Lohmann, Thèse de Doctorat, Université Louis Pasteur, Strasbourg, France, 2003.