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Crystallization-driven constitutional changes of dynamic polymers in response to neat/solution conditions†

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Dynamic polymers (dynamers) based on reversible imine interactions were generated and found to respond to changes in neat/solution environment, thus displaying adaptive behavior through modification of their constitution in order to maximize the stability of their mesoscopic state as a function of conditions.

Dynamic covalent chemistry (DCC),[1,2] the molecular wing of constitutional dynamic chemistry,[3] involves the generation of sets of molecular constituents from components linked through reversible interactions. The combination of polymer chemistry with DCC defines an area of constitutional dynamic polymer chemistry[4–6] and offers possibilities to develop adaptive materials.[3,7] Constitutional dynamic polymers, *dynamers*, are polymeric entities based on monomeric components connected through either reversible covalent bonds[4,6] or labile non-covalent interaction.[4,8] By virtue of the lability of these connections, they are constitutional dynamic materials capable of constitutional variation through exchange and reshuffling of their components. Consequently, dynamers may be expected to respond to external factors by shifting the equilibria of the system to the most stable state, allowing them to express or fine-tune a given property under different environmental conditions.[5c,f]

Amplification of a given dynamer of a dynamic combinatorial library (CDL) may be achieved by stabilizing its microscopic structures.[5c,f,6c] On the other hand, advantage may be taken of the mesoscopic features of dynamers. Thus, amplification of a given dynamer of a CDL under the pressure of a self-organization process,[9] such as the formation of an anisotropic phase, is of special interest. In principle, it can influence the library composition, favouring those species that form the most stable phase, such as solid state crystalline domains.

Here we describe our studies of constitutional dynamic polymers that are able to exchange and reshuffle their components through imine reversible bonding. As a consequence, these dynamers can adapt to different environmental conditions that stabilize/destabilize the mesoscopic states of the CDL members by generating different constitutional expressions.

The polymers **P1**–**P4**, which are connected through imine reversible bonds, have been obtained by polycondensation of the dialdehyde monomers **Ald1** or **Ald2** with the diamine monomers **Am1** or **Am2** in 1 : 1 molar ratios in the presence of anhydrous Na_2SO_4 in chloroform[10] (Fig. 1). ^{1}H-NMR spectroscopy confirmed the formation of the molecular polymers by the appearance of the corresponding imine proton signals (Fig. 2a–d). Polymer **P1**, which is the condensation material between **Ald1** and **Am2**, was an opaque solid giving an isotropic phase at 72.5 °C. **P2**, the material

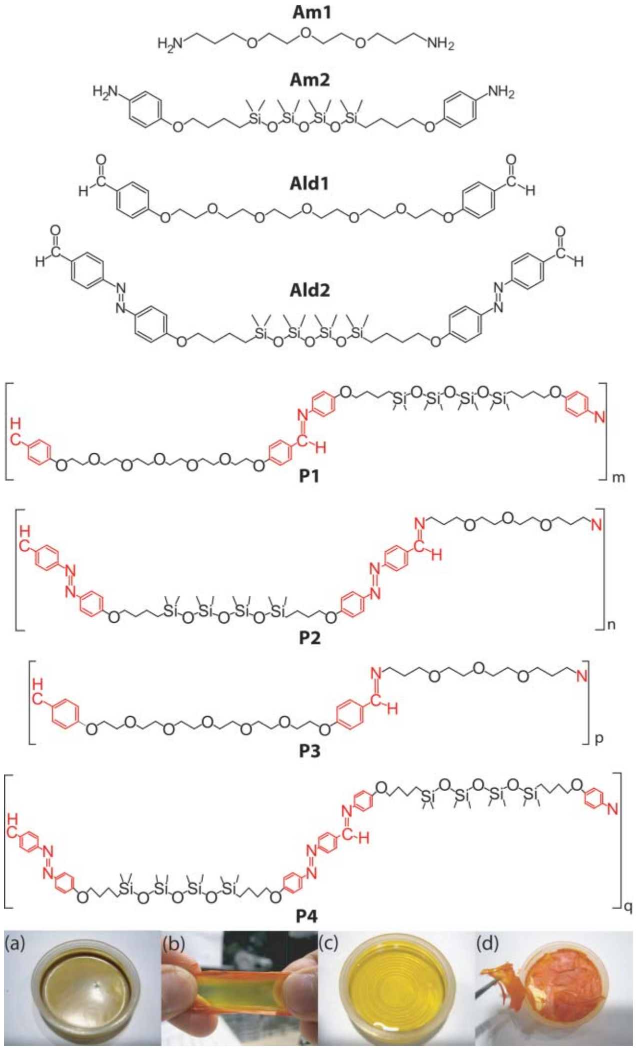

Fig. 1 (Top) Structure of the diamines **Am1** and **Am2**, of the dialdehydes **Ald1** and **Ald2** and of the polymers obtained by polycondensation: **P1** (**Ald1** + **Am2**), **P2** (**Ald2** + **Am1**), **P3** (**Ald1** + **Am1**) and **P4** (**Ald2** + **Am2**). The domains **P1d**, **P2d**, **P3d** and **P4d** are shown in red. "d" stands for domain of polymer. (Bottom) Physical aspect of the polymers (a) **P1**: opaque solid; (b) **P2**: stretchy film; (c) **P3**: viscous oil; (d) **P4**: brittle film.

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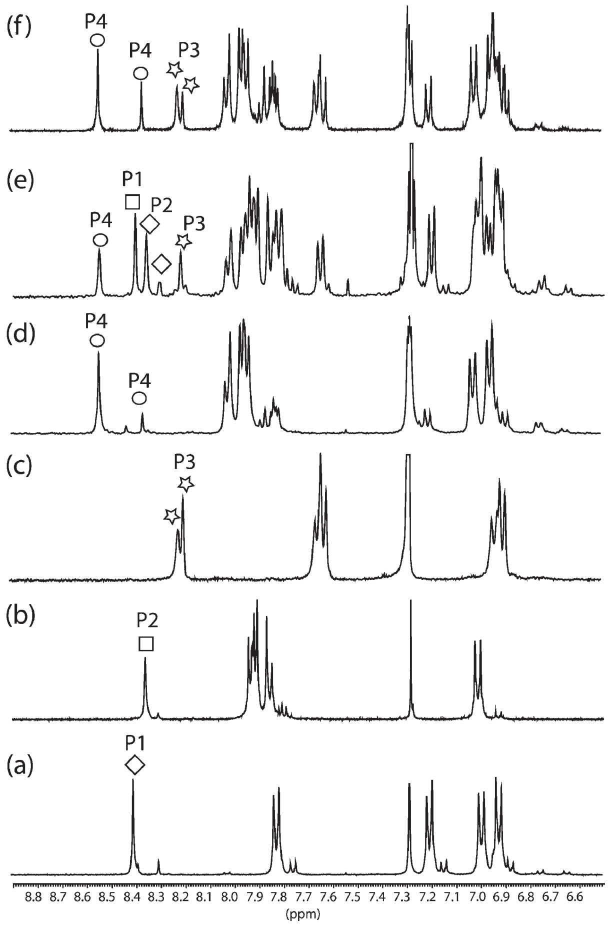


Fig. 2 Part of the ^{1}H-NMR spectra of polymers: (a) **P1**; (b) **P2**; (c) **P3**; (d) **P4**, (e) blend **Bl**$_{sol}$ and (f) blend **Bl**$_{neat}$ in $CDCl_3$ (*ca.* 5 mM) showing the C–H proton signals of the imine or aromatic groups. The symbols identify the characteristic proton signals of the reference polymers in the spectra of **B1**$_{sol}$ and **B1**$_{neat}$. The ^{1}H-NMR spectra were taken within 10 min after dissolving blend **Bl**$_{neat}$ in $CDCl_3$.

from **Ald2** and **Am1**, was obtained as a stretchy film, becoming an isotropic phase at 68.4 °C. **P3**, the condensation material between **Ald1** and **Am1**, was a viscous oil with an isotropic phase at less than 40 °C. **P4**, the material between **Ald2** and **Am2**, gave a brittle polymer film presenting the highest isotropic transition temperature at 159.6 °C because of the presence of strong mesogen. (Fig. 1) Integration of the very small remaining ^{1}H-NMR signal for terminal aldehyde protons gave a molecular weight of 34 000 g mol^{-1} ($\sim$50 repeating units) for **P3**. On the other hand, this signal was not observable for **P1**, **P2** and **P4**. The ratio between the signals of their new imine proton of the α-CH_2 of siloxane moiety for **P1**, **P2** and **P4** and the α-CH_2 of the oligo(ethylene oxa) moiety was exactly 2 : 4, indicating that polymerization had proceeded beyond the NMR detection limit. The molecular weights of these polymers were roughly estimated as $\geqslant$50 000 g mol^{-1} (using an ^{1}H-NMR detection limit of 1 mol%). The dynamic behavior of the present molecular polymers, resulting from the reversibility of the imine bonds, was demonstrated by the occurrence of ligand exchange and recombination, as shown by ^{1}H-NMR studies of polymer blends. Polymer blend **Bl**$_{sol}$ was prepared by just mixing solutions of the homopolymers **P1** and **P2** in $CDCl_3$ (*ca.* 5 mM) in equal molar ratio for 24 h with 1% pentadecafluorooctanoic acid (catalyst). Its ^{1}H-NMR spectrum showed four characteristic imine proton signals, which were assigned to (1) the connection between **Ald1** and **Am2**, *i.e.* **P1d** domain (at 8.42 ppm); (2) the connection between **Ald2** and **Am1**, *i.e.* **P2d** domain (at 8.36 ppm); most importantly, (3) a new connection between **Ald1** and **Am1**, *i.e.* **P3d** domain (at 8.23 ppm); and (4) another new connection between **Ald2** and **Am2**, *i.e.* **P4d** domain (at 8.57 ppm). **Bl**$_{sol}$ may thus be considered as a random copolymer resulting from recombination of all four components; it displays the four different domains in ratio **P1d** : **P2d** : **P3d** : **P4d** determined to be about 3 : 3 : 2 : 2 (Fig. 2e).

Most importantly, these dynamic features resulted in an adaptive behavior of the dynamer system. Indeed, blending of the parent dynamers, **P1d** and **P2d**, in neat conditions at 80 °C for 24 h gave **Bl**$_{neat}$. ^{1}H-NMR analyses allowed identification of the different constitutional changes of the blend **Bl**$_{neat}$ with respect to those of the blend **Bl**$_{sol}$. The spectrum of **Bl**$_{neat}$ showed only two characteristic imine proton signals, which were assigned to (1) a new connection between **Ald1** and **Am1**, *i.e.* **P3d** domain (at 8.23 ppm); and (2) another new connection between **Ald2** and **Am2**, *i.e.* **P4d** domain (at 8.57 ppm). Thus, under neat conditions, the dynamic system reshuffled and exchanged its components in a different way from the solution conditions. The percentage composition of **P1d** : **P2d** : **P3d** : **P4d** in the blend **Bl**$_{neat}$ was 0 : 0 : 5 : 5, revealing the presence of only the **P3d** and **P4d** domains, while the **P1** and **P2d** domains were repressed in the constitution of the system under neat conditions (Fig. 2f). In contrast, the formation of all four domains was obtained for **Bl**$_{sol}$.

Furthermore, subjecting **Bl**$_{sol}$ or **Bl**$_{neat}$ to successive sol–neat cycles by dissolution–solvent removal (evaporation) operations showed reversible switching between the **B1**$_{sol}$ and the **Bl**$_{neat}$ constitutional states without apparent fatigue (Fig. 3).

The constitutional evolution of the dynamic polymer systems can be explained by the formation of the crystalline copolymer **P4** in the CDL (Scheme 1). Under the neat conditions at 80 °C, **P1**,

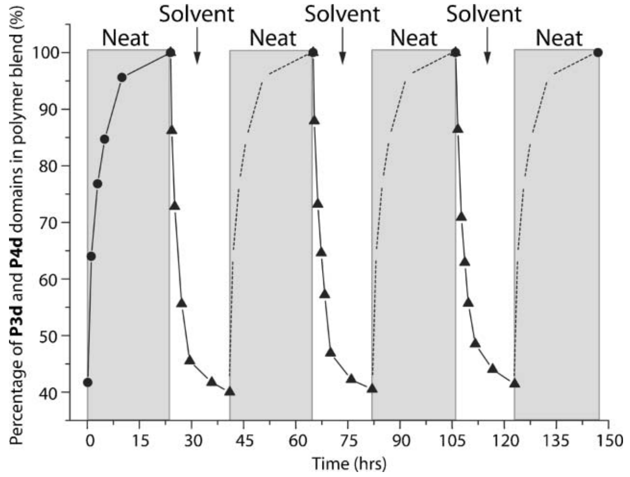
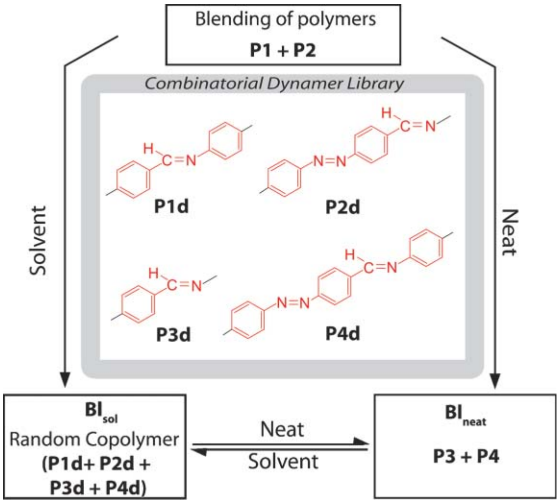


Fig. 3 Constitutional dynamic interconversion between the polymer blends **Bl**$_{sol}$ in solution and **Bl**$_{neat}$ in neat conditions. The percentages of **P3d** and **P4d** domains are calculated from the integration of the imine CH ^{1}H-NMR signals of the blends in $CDCl_3$ (*ca.* 10 mM). At 100%, the composition is that of **Bl**$_{neat}$ (**P3** + **P4**). The ^{1}H-NMR spectra were taken within 10 min after dissolving blend **Bl**$_{neat}$ in $CDCl_3$.



Scheme 1 Schematic representation of adaptive behavior of the dynamic polymer system in response to a change in physical state: solution and neat acting as stimuli.

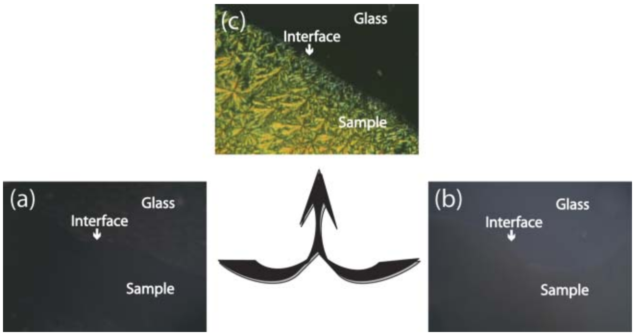


Fig. 4 Photographs taken with a polarized light microscope in transmission mode (×40) at 80 °C: (a) isotropic phase of homopolymer **P1** at 80 °C, (b) isotropic phase of homopolymer **P2** at 80 °C and (c) anisotropic phase of polymer blend **Bl$_{neat}$** (**P3** + **P4**) at 80 °C.

P2, **P3** and the mixed polymers existed as isotropic liquids, while **P4** was the only crystalline member. This strong driving force shifted the equilibria of the CDL towards **P4** and, as consequence, generated also agonistically[11] the copolymer **P3**. As shown in Fig. 4, both neat parent dynamers, **P1** and **P2**, existed as isotropic liquids at 80 °C, while an anisotropic phase grew up after stacking them together in the same conditions. On the other hand, when the polymer blend **Bl$_{neat}$** was dissolved in an organic solvent, the dissolution of the crystalline phase allowed the dynamic system to re-adapt, reshuffle and re-exchange the monomers so as to generate the four imine domains of **P1**, **P2**, **P3** and **P4**.

The processes described here present several aspects of adaptive behavior in a system of covalent dynamic polymers in response to a change in physical state (Scheme 1).

(1) The parent dynamers **P1** and **P2** generated two offspring dynamer blends, a random copolymer **Bl$_{sol}$** when mixed in solution, and a mixture **Bl$_{neat}$** of the two polymers **P3** and **P4** in neat conditions.

(2) This adaptive behavior is retained in the generation of the offspring systems **B1$_{sol}$** and **Bl$_{neat}$**, which can be reversibly switched over several dissolution–evaporation cycles.

(3) Formation of **Bl$_{sol}$** from (**P1** + **P2**) or from **Bl$_{neat}$** amounts to a randomization giving a copolymeric material containing all four monomeric components **Am1**, **Am2**, **Ald1** and **Ald2**.

(4) Formation of **Bl$_{neat}$** from the **Bl$_{sol}$** random copolymer in the neat state upon solvent removal amounts to a derandomization giving a mixture of only the polymers **P3d** and **P4d**. This implies a process of *self-selection* under the pressure of the formation of an organized phase, the crystalline copolymer **P4**.

(5) The system described here represents a constitutional dynamic material displaying adaptive behavior by constitutional dynamic interconversion between two constitutional states in response to a change in physical stimuli ("solution" or "neat" conditions).

The present results demonstrate the generation of dynamic imine polymers displaying constitutional dynamics by reorganization and exchange of the monomers in the polymer chains through bond recombination between their dialdehyde and diamine components. More importantly, these dynamers can adapt to different environmental conditions that stabilize/destabilize the mesoscopic states of the CDL members. Last but not least, the dynamic selection processes can be reversibly switched over several interconversion cycles without significant fatigue. In more general terms, dynamers belong to a class of materials that may respond to chemical effectors or physical stimuli by constitutional variation, *i.e.* adaptive materials.

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10 Synthetic procedures and compounds will be described in detail in a full paper. All new compounds have been characterized by the usual spectroscopic and analytical techniques.

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