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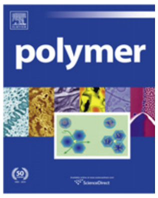

# Effect of self-complementary motifs on phase compatibility and material properties in blends of supramolecular polymers

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ABSTRACT

Applicability of supramolecular polymers blending in preparation of materials with tunable properties is reported. The effect of strongly dimerising 2-ureido-4[1*H*]-pyrimidinone (UPy) end groups on phase compatibility in binary polymer blends was studied. A low molecular weight poly(tetrahydrofuran) diol was functionalized with UPy moieties (PTHF(UPy)$_2$, a soft material) and mixed with varying amounts of low molecular weight UPy functionalized polycaprolactone di- and triol (PCL(UPy)$_2$ and PCL(UPy)$_3$, both relatively strong and stiff materials). Thermal studies showed that $T_g$ of the homopolymers shifted to intermediate temperatures. AFM observation suggested that the phase domain decreased significantly after UPy functionalization of diols. Also the mechanical properties improved at a higher rate than those predicted by the rule of mixtures. These findings indicate that blend components are placed in intimate contact as a result of the UPy–UPy interactions. The reversible crosslinking by PCL(UPy)$_3$ gave better control still over the mechanical properties of the supramolecular polymer blends.

## 1. Introduction

Production of blends or alloys through simply mixing two or more homo- or copolymers is a well-known strategy for achieving a specific portfolio of physical properties without need for sophisticated synthetic procedures [1]. Due to the inherent high molecular weights of polymers, the thermodynamics of mixing usually do not allow for mutual solubility, consequently, two distinct phases are formed. These inevitable macrophase separated structures with phase domains ranging between a few microns and tens of microns are of great interest for their novel properties (such as scaffold preparation in biomedical applications)[2] whereas the relatively large phase domain and very poor interfacial interaction often results in unacceptable properties. For instance, micron size phase domains result in structural inhomogeneities sensed by cells in biomedical devices and especially scaffolds for tissue engineering applications. In recent years, considerable efforts have been invested in improving the phase miscibility of polymer blends through supramolecular approaches. Correlating the composition with properties of the blend and processing requirements remains the major challenge from a technological point of view [3]. The mixing behavior of two dissimilar polymers can be evaluated with Flory–Huggins theory[4,5], which provides an expression (Equation (1)) for the change in Gibbs free energy ($\Delta G_m$) upon mixing two polymers, A and B:

$$\frac{\Delta G_m}{RT} = \frac{\Phi_A}{M_A}\ln \Phi_A + \frac{\Phi_B}{M_B}\ln \Phi_B + \chi_{AB}\Phi_A\Phi_B \qquad (1)$$

where $\Phi_A$ and $\Phi_B$ and $M_A$ and $M_B$ are the volume fraction and the degree of polymerization of polymers A and B, respectively. $\chi_{AB}$ is the Flory–Huggins interaction parameter in this equation. The necessary condition for miscibility is therefore $\Delta G_m < 0$. Considering the high molecular weights of macromolecules, the entropic term of the free energy becomes negligibly small and the main driving force for miscibility will be the enthalpic term of the equation. Therefore, the miscibility of polymers can be explained based on the favorable and unfavorable interactions between the blend components. Two main strategies are often used to improve poor interfacial interaction in multiphase polymeric systems. As the first strategy, a di- or multiblock copolymer is added to a binary polymer blend as an interfacial modifier [6–9]. Long chain multiblock copolymers have been shown to concentrate at the interfaces in biphasic blend systems and strengthen the interface through formation of entanglements with each homopolymer [10]. In a second approach, blend components are functionalized with special groups to introduce intermolecular interactions (such as hydrogen bonding) to the blended system and

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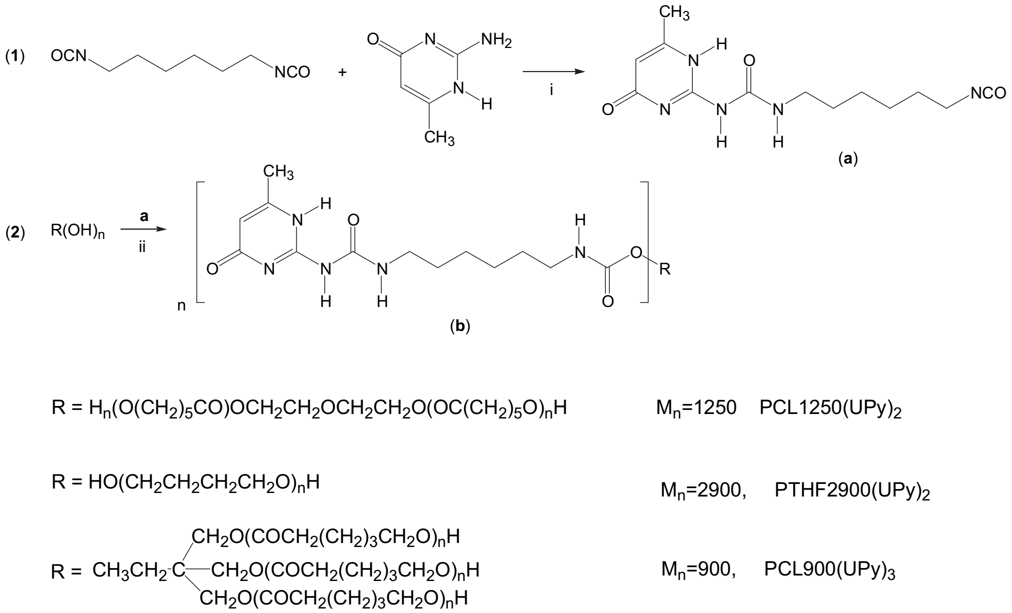

**Scheme 1.** Synthesis of supramolecular polymers based on poly(caprolactone) and poly(tetrahydrofuran). 1. Synthesis of NCO precursor (a, Yield = 96%), i = 100 °C, 20 h; 2. Synthesis of PCL1250(UPy)$_2$, PTHF2900(UPy)$_2$ and PCL900(UPy)$_3$; Yield = 70, 75, and 68%, respectively), ii = 60 °C, CHCl$_3$, DBTDL, 16 h.

decrease the interfacial tension. The blends of functionalized homopolymers exhibit a morphology similar to that of the covalently bonded block copolymers.

The effect of hydrogen bonding on interfacial properties and therefore the blend properties has become the subject of numerous studies [11,12]. Severe control over the microstructure of the polymer components is required to optimize the amount of intermolecular hydrogen bonding [10]. However, a minimum associative energy of $10^3$ mol$^{-1}$ or higher is required for a microphase separated biphasic system to become miscible [13]. Therefore, multiple hydrogen bonding units with extremely high dimerization constants ($K_{dim}$) are appealing to material scientists for the preparation of polymer blends with tunable properties. The degree of polymerization in such systems can then be controlled by concentration or temperature. This approach benefits from the potential for low processing temperatures and may result in mixing at the molecular level. To achieve desired blends through supramolecular approaches two methods have been exploited; functionalization of homopolymers with complementary [13–17] or self-complementary [18] hydrogen bonding moieties. Heterodimerization of complementary associating groups at the termini of two different homopolymers, often results in the formation of pseudo block copolymers as implied from a single glass transition temperature observed for such mixtures [17]. However, the degree of polymerization is highly influenced by the stoichiometric balance in copolymer formation based on functionalization of low molecular weight building blocks with complementary associating groups. In the second method, two supramolecular polymers with self-associating groups (such as UPy groups with a dimerization constant $\sim 5 \times 10^7$ l mol$^{-1}$ in chloroform[19]) at both ends are mixed to produce materials with composition-dependent mechanical properties [18,20]. A third route was also introduced in which low molecular weight A-B type copolymers were functionalized with self-associating groups to produce supramolecular (random) copolymers. However, it has been shown that changes in mechanical properties of these copolymers are not completely composition dependent [20].

The UPy modified polymers are distinguished from the conventional polymers by excellent bulk properties and ease of processing due to their low melt viscosities, which makes them suitable materials in different applications from printing to tissue engineering [21,22]. It has been shown that these self-complementary moieties afford a higher degree of polymerization (in chloroform and above the critical polymerization concentration, e.g. between 1 and 100 mM L$^{-1}$) compared to complementary hydrogen bonding units [15]. Hence, functionalization of telechelic polymers with self-complementary UPy groups for preparation of materials with tailored properties is extremely appealing in materials research.

Anthamatten has used a mean field model to predict the effect of end functionalization of telechelic polymers with complementary and self-complementary groups on the polymer–polymer miscibility changes [23]. In that study the Flory-Huggins mixing theory was modified with Painter's association model to account for the equilibrium self associating end groups. Considering input parameters such as the polymer chain length, a temperature dependent interaction parameter and a temperature dependent equilibrium constant Anthamatten's main field model predicted that two phase regions were stabilized by self complementary interactions. Wrue et al. studied the miscibility changes in PS/PMMA blends where both polymers where functionalized with UPy groups at both ends. The results in their study indicated two phase regions were formed across the entire composition range [24]. Feldman et al. have studied the effect of multiple hydrogen bonding (MHB) end groups on the phase behavior in blends of (meth)acrylic polymers [17]. The UPy and 2,7-diamido-1,8-naphthyridine (NAPy) end groups have been utilized to produce UPy–UPy self complementary or UPy–NAPy complementary interactions in the blends of Upy functionalized poly benzyl methacrylate (PbnMAUPy) with NAPy functionalized poly n-butyl acrylate (PnBANAPy). Considering the thermal and microscopic experiments results they concluded that the MHP functionalization results in enhanced phase compatibility in the UPy–UPy self complementary or UPy–NAPy complementary systems. The effect was attributed to the formation of diblock species at the homopolymer–homopolymer interfaces. However, the relative amount of the diblock was estimated to be less in the UPy–UPy system due to the ability of the UPy groups to strongly homodimerize. It has been shown that the phase behavior in such multiply hydrogen bonded systems is strongly influenced by the molecular weight of the blend components as well as the temperature [25].

To the best of our knowledge, the effect of phase compatibilization through UPy functionalization on the bulk properties of supramolecular polymer blends has been studied merely for (miscible) blend preparations from homopolymers of the same or very similar backbones (for example, mixtures of supramolecular polycaprolactones or blends of polyvalerolactone/polycaprolactone [18,20]). In this report, we address the effect of UPy functionalization on the end use properties (e.g. mechanical and dynamic mechanical properties) of supramolecular polymer blends from telechelic polymers with completely different polymeric backbones. Polytetrahydrofuran diol (a polyether), polycaprolactone diol (a polyester) and polycaprolactone triol (a polyester) are end capped with UPy groups and used as model compounds to explore the effect of self associating functionalities/physical crosslinking on the mechanical, dynamic mechanical and morphological behaviour of their blends. The structure of supramolecular polymer blends composed of complementary hydrogen bonding arrays is comparable to that of an alternating (block) copolymer, whereas supramolecular polymer blends in the present study are more likely to resemble the structure of segmented copolymers.

## 2. Experimental

### 2.1. Materials

Poly(tetrahydrofuran) diol (PTHF2900$(OH)_2$, $M_n = 2900$ g/mol), poly(caprolactone) diol (PCL1250$(OH)_2$, $M_n = 1250$ g/mol), and poly (caprolactone) triol (PCL$(OH)_3$, $M_n = 900$ g/mol), 2-amino-4-hydroxy-6-methylpyrimidine, 1,6-diiso-cyanatohexane and dibutyl tin dilaurate (DBTDL) were obtained from Aldrich.

### 2.2. Synthesis

Supramolecular polymers PTHF2900$(UPy)_2$, PCL1250$(UPy)_2$ and PCL900$(UPy)_3$ were synthesized by end capping poly(tetrahydofuran) diol (PTHF2900$(OH)_2$), poly(caprolactone) diol (PCL1250 $(OH)_2$), and poly(caprolactone) triol (PCL$(OH)_3$), respectively, with UPy functionalities in two steps as described in the literature (Scheme 1) [26].

### 2.3. Blend preparation

A solution mixing approach was taken to blend the supramolecular polymers. Blend components were co-dissolved in chloroform by stirring in the solvent (10 mg/ml) at 30 °C for 5 h. The solvent was evaporated at room temperature, overnight and the blends were then dried for 48 h at reduced pressure at 30 °C. Blend composition ratios of 0/100, 25/75, 50/50, 75/25 and 100/0 (mol%) were prepared for the supramolecular polymer pairs of PTHF2900 $(UPy)_2$/PCL1250$(UPy)_2$ and PTHF2900$(UPy)_2$/PCL900$(UPy)_3$. The blends were studied for chemical (FT-IR), thermal (DSC), mechanical (tensile), dynamic mechanical (DMTA) and morphological (AFM) properties.

### 2.4. Analytical methods

$^1H$ NMR and $^{13}C$ NMR were recorded on Brucker 400 or 500 MHz. Chemical shifts are given in ppm ($\delta$) values relative to tetrahydrosilane (TMS). ATR-FTIR spectra were recorded on a Perkin–Elmer spectrometer with ATR sampling accessory. FT-IR spectra were recorded on a Bruker spectrometer. Samples were prepared for FT-IR by solvent casting on KBr.

Differential scanning calorimetry (DSC) experiments were carried out on Perkin–Elmer Pyris 1 instrument equipped with cryogenic system for subambient temperature measurements. Samples of 10–12 mg were measured under nitrogen atmosphere in the temperature range of 90–110 °C with heating and cooling rates of 20 and 100 °C $min^{-1}$; the data reported here were taken from the second heating run. AFM was performed in tapping mode on thin films of blend samples (spin coated at 2500 rpm from a chloroform solution, 10 mg/ml) on silicone wafer (washed with acetone and purged with $N_2$) at room temperature with a Digital Instrument Multiple Nanoscope IV using silicon cantilever tips. A scan rate of 0.5 Hz was used. The spin coated samples were stored for 24 months at room temperature and inspected with AFM (Dual Scope-DME) in non-contact mode. A constant force of 42 N $m^{-1}$ was applied. Mechanical properties were studied with stress–strain measurements carried out on an MTS universal tensile machine at an elongation rate of 0.5 mm $min^{-1}$ with a load cell of 200 N. Tensile dumbbells with a cross section area of 1.5 $mm^2$ were punched out of sheets of materials prepared by compression molding at 90 °C and 20 MPa. The gage length or length between the clamps was set at 10 mm. A minimum number of 4 samples were evaluated to determine Young's modulus, peak stress and strain at break. Tensile modulus was always calculated at the initial linear part of the strain-stress curve [27,28] using the Equation 2 (Hook's law):

$$\sigma = E\epsilon \quad (2)$$

Where $\sigma$ and $\epsilon$ are stress and strain, respectively. $E$ relates stress to strain and for simple extension is called Young's modulus. The dynamic mechanical thermal (DMTA) data were collected on a Triton instrument in oscillating bending mode (single cantilever with the length between clamps of 5 mm). Rectangular bars of $14 \times 7 \times 0.7$ $mm^3$ were compression molded at 90 °C and 20 MPa and studied at a fixed frequency of 1 Hz and displacement of 0.05 mm. The temperature was scanned between −100 and 40 °C by steps of 4 °C $min^{-1}$.

## 3. Results and discussion

### 3.1. Synthesis of PTHF2900$(UPy)_2$, PCL1250$(UPy)_2$ and PCL900 $(UPy)_3$

PTHF2900$(UPy)_2$ is a thermoplastic elastomer and showed a glass transition at about −78 °C and one melt transition at about 26 °C. These properties are remarkably different from those reported for PTHF1000$(UPy)_2$ mainly due to the presence of a telechelic polymer having higher molecular weight in the supramolecular polymer backbone [29]. Non-modified PCL1250$(OH)_2$, a waxy solid, is characterized with two melt transitions at 36 and 44 °C. PCL1250$(UPy)_2$ on the other hand is a polymer with one glass transition temperature at ca. −63 °C and two melt transitions at ca. 40 and 74 °C. PCL1250$(UPy)_2$ is known as a phase separated polymer and the endothermic peaks in its DSC trace are attributed to the melting of the polyester backbone and the UPy dimers [20,30]. The melt transition of PCL1250$(UPy)_2$ occurs at a significantly higher temperature than conventional PCL ($M_n = 65$ kg/mol, $T_m = 56$ °C) suggesting that stable crystallites were formed from (lateral) stacking of UPy–UPy dimers [30]. PCL900$(UPy)_3$ demonstrates completely different material properties from the PCL900 $(OH)_3$ building block. The telechelic triol is a viscous liquid whereas the UPy-functionalized supramolecular polymer, PCL900$(UPy)_3$, is a strong and stiff solid and shows a clear glass transition temperature at around −22 °C. The melt transition peak of this polymer appears at 93 °C in the DSC trace. The melt temperature and glass transition observed for PCL900(UPy)$_3$ are in good agreement with values previously reported in literature [31].

### 3.2. Supramolecular polymer blends

#### 3.2.1. PTHF2900(UPy)$_2$/PCL1250(UPy)$_2$

Blend investigations were started by combining UPy functionalized low molecular weight poly(tetrahydrofuran), PTHF2900 (UPy)$_2$, with UPy functionalized low molecular weight poly(caprolactone), PCL1250 (UPy)$_2$, into so-called segmented copolymers as displayed in Fig. 1. In contrast to the telechelic PTHF2900(OH)$_2$ and PCL1250(OH)$_2$ (both waxy solids), supramolecular polymers PTHF2900(UPy)$_2$ and PCL1250(UPy)$_2$ are both thermoplastic elastomers. Mixtures of 1:3, 1:1 and 3:1 (molar ratio) of these polymers are clear, macroscopically homogeneous solids and exhibit entirely different appearance from their building blocks.

*3.2.1.1. Thermal properties.* DSC experiments were run on the materials and the results are summarized in Table 1. All data given in the table are from the second heating runs, which reflect the intrinsic thermal properties of the homopolymers/polymer blends.

As can be seen in Table 1, the glass transitions of PCL1250(UPy)$_2$ and PTHF2900(UPy)$_2$ shifted towards intermediate temperatures in their position with the blend composition.

Interestingly, the blends PTHF2900(UPy)$_2$/25% PCL1250(UPy)$_2$ and PTHF2900(UPy)$_2$/75% PCL1250(UPy)$_2$ have glass transitions appearing at about −77 and −60 °C, respectively. The blend with 50 mol% of each component showed two distinct glass transitions at −77 and −64 °C. The specific heat capacities at glass transitions were measured as 1.58 and 0.35 J/(g.K) for PTHF2900(UPy)$_2$ and PCL1250(UPy)$_2$ homopolymers, respectively. However, the corresponding heat capacity of PTHF2900(UPy)$_2$ in the blend PTHF2900 (UPy)$_2$/25% PCL1250(UPy)$_2$ decreased significantly (0.36 J/(g.K) for the transition at about −77 °C). It is likely that chain motions of PTHF2900(UPy)$_2$ above $T_g$ were hindered by the segments of PCL1250(UPy)$_2$ that remained in a frozen-in state at this low temperature region.

**Table 1**
Glass transition temperatures, heat capacities, melt transitions and heat of fusion of the UPy functionalized PTHF2900 and PCL1250 polymers and their blends.

| Polymer | $T_g$ (°C)[a] | $\Delta C_p$ J/(g.K) | $T_m$ (°C) | $\Delta H_m$ J/g |
|---|---|---|---|---|
| PTHF2900(UPy)$_2$ | −78.8 | 1.58 | 23.9 | 45.5 |
| PTHF(UPy)$_2$/25% PCL(UPy)$_2$ | −77.0 | 0.36 | 23.0,59.0 | 23.1,2.4 |
| PTHF(UPy)$_2$/50% PCL(UPy)$_2$ | −76.8,−63.7 | 0.16,0.15 | 24.5,58.2,69.9 | 14.2,2.9[b] |
| PTHF(UPy)$_2$/75% PCL(UPy)$_2$ | −60.2 | 0.20 | 25.4,72.4 | 20.1,3.1 |
| PCL1250(UPy)$_2$ | −57.8 | 0.35 | 39.2,74.5 | 19.2 |

DSC data was taken from the second heating run.

[a] $T_g$ was measured as the onset of the specific heat changes in the DSC trace.

[b] Total for two peaks at 58 and 70 °C.

Inspection of the melting peaks provided more information on the structural changes upon blending. The melting temperature of PTHF2900(UPy)$_2$ remained more or less unchanged in the blends. The melting behavior of PCL1250(UPy)$_2$, however, was affected by the blend composition. The endothermic transition of PCL1250 (UPy)$_2$ at 39 °C was suppressed in the blends suggesting that the crystallinity of the PCL backbone was affected by the presence of PTHF2900(UPy)$_2$. The IR absorption bands at 1724 and 1737 cm$^{-1}$ are typical of the crystalline and amorphous vibrations of carbonyl groups in polyesters, respectively [32,33]. A closer look at the deconvoluted peaks in the IR spectra of PCL1250(UPy)$_2$ and the blends showed that the relative intensity of the crystalline vibration of C=O at 1724 cm$^{-1}$ decreased in the blends (Fig. 2). Thus, endothermic peak suppression at 39 °C in the DSC trace of the blends can be attributed to the reduced crystallinity of the polyester backbone in presence of PTHF2900(UPy)$_2$.

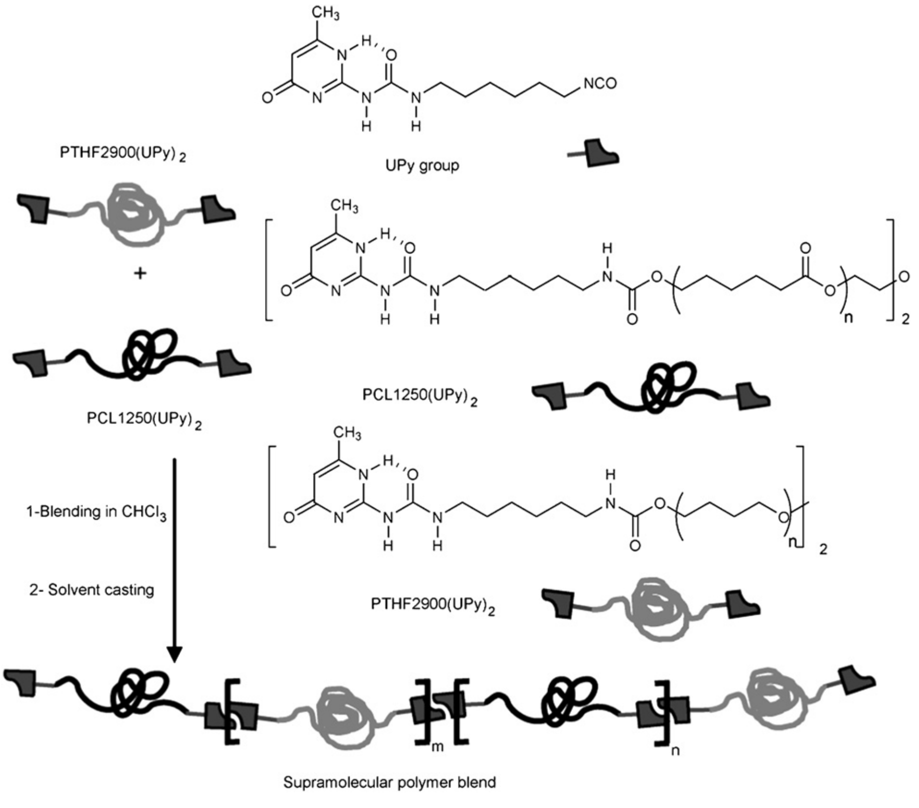

**Fig. 1.** Schematic display of supramolecular blend structure based on PTHF2900(UPy)$_2$ and PCL1250(UPy)$_2$.

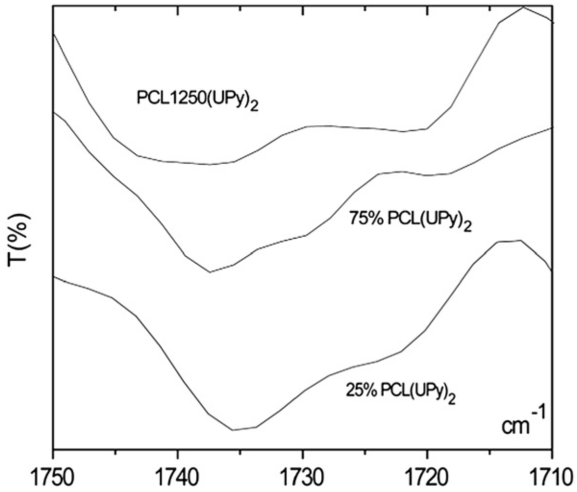

**Fig. 2.** Carbonyl stretching region of PCL1250(UPy)$_2$ and blends with 75 and 25 mol% of this component at room temperature. The intensity of the crystalline and amorphous vibrations of carbonyl group at 1724 and 1737, respectively, changed as the amount of PTHF2900(UPy)$_2$ in the blends increased.

The melt transition of PCL1250(UPy)$_2$ in the blend PTHF2900(UPy)$_2$/25% PCL1250(UPy)$_2$ shifted to a significantly lower temperature (59 °C) and two distinct melt transitions were observed for the equimolar mixture of the two homopolymers (appeared at about 58 and 69 °C). Emergence of a second melting peak for PCL1250(UPy)$_2$ in this blend can be possibly due to formation of a new PTHF2900(UPy)$_2$ enriched PCL1250(UPy)$_2$ phase in the blend. Again a single endotherm was recorded for PCL1250(UPy)$_2$ component in the blend PTHF2900(UPy)$_2$/75% PCL1250(UPy)$_2$ (at about 72 °C). Relatively high melting temperatures of the supramolecular polymer/polymer blends (compared to the telechelic PCL1250(OH)$_2$ at 40 °C) was attributed to the microphase separated domains of UPy dimers [30,34].

Blends of PCL(UPy)$_2$ with UPy functionalized poly(valerolactone) (PVL(UPy)$_2$) were studied and it was reported that the size of crystallites formed from UPy dimers was affected by the crystallinity of the polymeric backbone [21]. In a separate study, PCL(UPy)$_2$ polymers were synthesized from PCL(OH)$_2$ of different molecular weights (2.2, 3.7 and 7 kg/mol) and thermal analysis of the resulting supramolecular polymers showed that the crystallinity of the polymer backbone decreased in presence of UPy moietie [30]. Therefore, suppression of the melt transition of the PCL backbone in the supramolecular polymer blends can possibly be due to formation of thicker lamella (originated from stacking of the UPy–UPy dimers). Formation of more stable crystallites as a result of UPy–UPy stacking is also evident by a +13 °C shift of the highest melt transition corresponding to PCL1250(UPy)$_2$ when the amount of this component in the blends increased from 25 to 75%. For comparison, mixtures of PTHF2900(OH)$_2$ and PCL1250(UPy)$_2$ of similar compositions to the supramolecular polymer blends were prepared and studied for the thermal properties. No meaningful shifts were observed for the melting temperatures of the corresponding low molecular weight diols in the blends. A glass transition temperature was not registered for the telechelic diols or their mixtures.

These results lead to the conclusion that in the melt state, phase separation between the blend components is not sufficient to allow the separate phases to behave as they would in isolation. In other words, in the supramolecular polymer blends that were studied each phase affects the other.

*3.2.1.2. Atomic force microscopy.* Room temperature AFM was used to study the morphological changes upon blend preparation from PTHF2900(UPy)$_2$ and PCL1250(UPy)$_2$ supramolecular polymers (Fig. 3). A PTHF2900(OH)$_2$/50% PCL1250(OH)$_2$ blend was also prepared and studied with AFM (Fig. 3A) to explore the effect of UPy functionalization on phase morphology of the supramolecular blends. From the micrograph Fig. 3A it can be seen that 50/50 mixture of telechelic diols adopted a dispersed phase-matrix structure with phase domains varied from several hundred nanometers up to a few microns. Both the PTHF2900(UPy)$_2$/25% PCL1250(UPy)$_2$ and PTHF2900(UPy)$_2$/75% PCL1250(UPy)$_2$ blends are characterized by dispersed particle type of morphology in the form of nanosized (more or less) spherical domains. Interestingly, the average domain size decreased significantly (to about 10–50 nm) for these blends compared to the mixture of telechelic diols. The phase structure was slightly different for the blend PTHF2900(UPy)$_2$/50% PCL1250(UPy)$_2$.

A so-called co-continuous morphology is expected for 50/50 mixtures of homopolymers especially when the interfacial tension between phases is fairly low [35]. In fact, the dispersed phase started to elongate in the 50/50 blend (above the percolating concentration) as is clearly seen in Fig. 3C, although formation of a fully co-continuous structure in this composition is not clear from the micrograph. The weight ratio of the blend components deviates from 50/50 (because of different molecular weights of the building blocks). The phase domain in the 50/50 (molar ratio) blend of the two homopolymers is still below 50 nm. These blends are classified as microcomposites in which the dimensions of the phases lie below 100 nm [1]. Similar phase domains (14 nm, measured with SAXS and TEM) were reported for a so-called pseudo block supramolecular copolymer formed from poly(etherketone, PEK) and poly(isobuthylene, PIB) joined through multiple hydrogen bonds between a complementary associating “Hamilton” receptor on one block and barbituric acid on the second block [13]. It is evident from AFM observations that UPy functionalization gives rise to fine dispersion of the minor phase in the matrix and that mixing occurred at a nano scale. This finding is perfectly in line with the prediction for the morphology of polymer blends that properties of multiphase polymer blends are mainly dependent on the interfacial chemistry [36,37]

Samples were stored at room temperature for 24 months and studied by AFM for potential changes in the phase domain (Fig. 3E–G). No significant changes were observed in the phase domain as is clearly seen in Fig. 3 D–G.

*3.2.1.3. Mechanical and dynamic mechanical properties.* Mechanical properties of a polymer blend are controlled by several factors such as the properties of the blend components, the phase morphology and the interphasial adhesion. The two latter factors are important from the viewpoint of stress transfer within the blend. Therefore, we studied the mechanical properties of our supramolecular blends next. Variations in the tensile modulus, tensile strength and elongation at break with blend compositions as well as the representative stress-strain curves are displayed in Fig. 4. PCL1250(UPy)$_2$ is a brittle material (as evidenced by the elongation at break of about 20%) with a relatively high Young's modulus (about 35 MPa). PTHF2900(UPy)$_2$ on the other hand, elongates about 90% before it breaks and has a modulus of ca. 8 MPa.

The elastic modulus increased and elongation at break decreased as the concentration of the stiffer component PCL1250(UPy)$_2$, increased in the blends. Surprisingly, the break stress increased significantly (nearly 2-fold) when 25% PCL1250(UPy)$_2$ was added to PTHF2900(UPy)$_2$ and only a slight increase in the tensile stress was obtained for the blends with larger amounts of PCL1250(UPy)$_2$. The relatively high tensile stress of the blends might be ascribed to the increased force required for chain pull-out from stabilized hard segments as discussed before. Elastic modulus

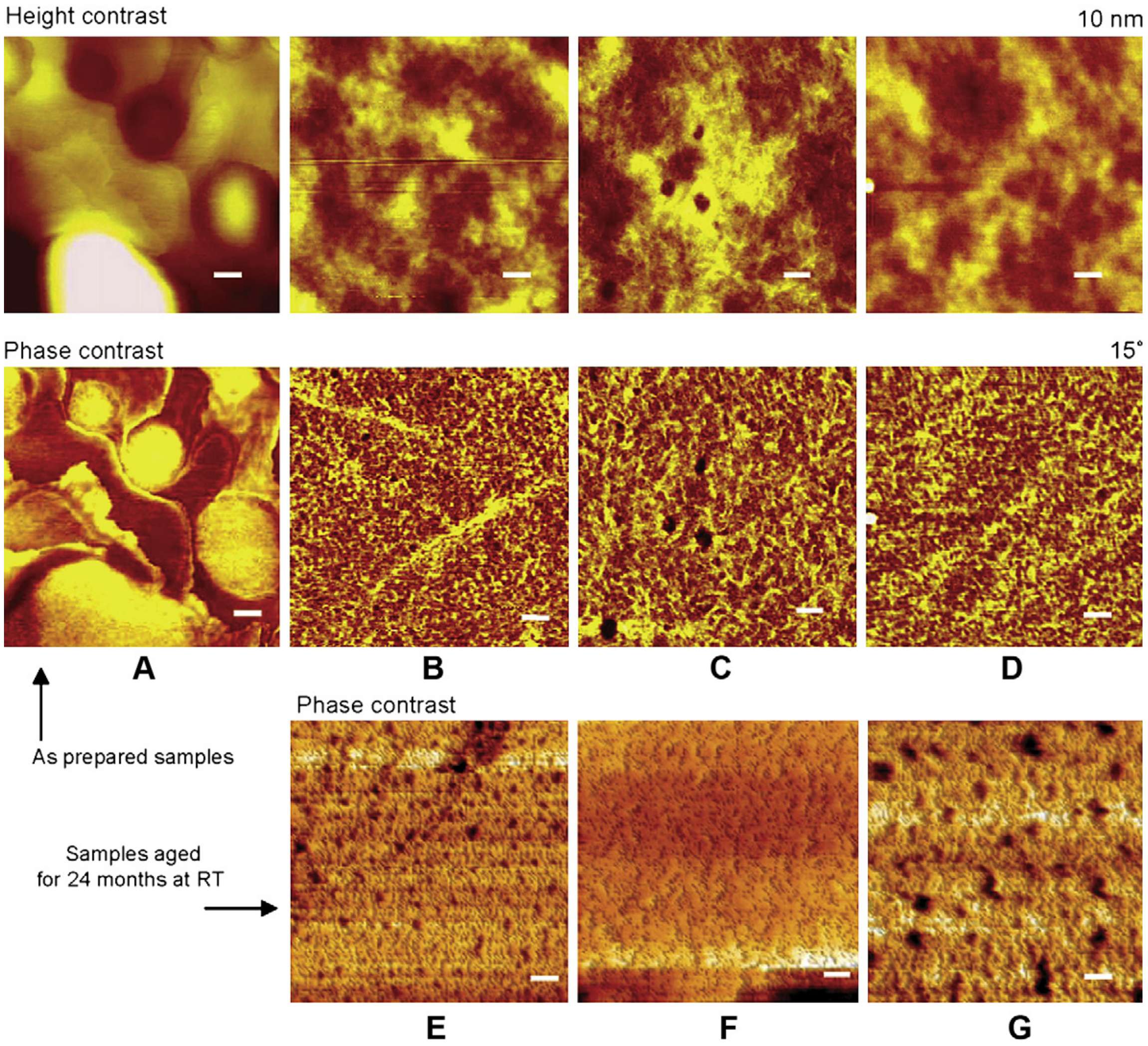

**Fig. 3.** A–D; Tapping mode AFM images of as prepared A: PTHF2900$(OH)_2$/50% PCL1250$(OH)_2$, B: PTHF2900$(UPy)_2$/25% PCL1250$(UPy)_2$, C: PTHF2900$(UPy)_2$/50% PCL1250$(UPy)_2$ and D: PTHF2900$(UPy)_2$/75% PCL1250$(UPy)_2$ composites (at room temperature). E–G; non-contact mode AFM images of the samples after 24 months at room temperature E: PTHF2900 $(UPy)_2$/25% PCL1250$(UPy)_2$, F: PTHF2900$(UPy)_2$/50% PCL1250$(UPy)_2$ and G: PTHF2900$(UPy)_2$/75% PCL1250$(UPy)_2$. All pictures are of the same magnification and scale bars represent 100 nm.

of polymer blends can be roughly estimated based on a simple *rule of mixtures* (Equation (2)) [1]:

$$E_b = E_1\varphi_1 + E_2\varphi_2$$

Where $E_b$, $E_1$ and $E_2$ are the Young's moduli of the blend and the individual blend components 1 and 2, respectively. $\varphi_1$ and $\varphi_2$ represent the corresponding volume fractions of the blend components. The experimentally measured value of modulus for each blend was about 10% higher than the calculated value, which can be attributed to the strong interfacial interaction.

Dynamic mechanical properties of the supramolecular polymers/polymer blends were also studied. Homopolymers PTHF2900 $(UPy)_2$ and PCL1250$(UPy)_2$ have storage moduli of about 13 and 20 MPa, respectively, at room temperature as is depicted in Fig. 4D. The storage modulus of PTHF2900$(UPy)_2$ decreased gradually with temperature (starting from −100 °C) from glass to rubber and finally the material yielded at around 18 °C, which is the melting point of the polymer as was indicated by the DSC experiment. Two distinctions became apparent between PCL1250$(UPy)_2$ and PTHF2900$(UPy)_2$; first a lower storage modulus was observed for the former above $T_g$ and second the polymer yielded at a higher temperature of 30 °C. $T_g$ and $T_m$ values of both the polymers agree nicely with the data from DSC (Table 1). Storage modulus of the blend PTHF2900$(UPy)_2$/50% PCL1250$(UPy)_2$ is between the two homopolymers and still a higher modulus was registered for the blend PTHF2900$(UPy)_2$/75% PCL1250$(UPy)_2$. No yielding behavior was observed for these blends as was expected from the endothermic peak suppression in the DSC trace (Table 1).

### 3.2.2. PTHF2900$(UPy)_2$/PCL900$(UPy)_3$

Versatility of the supramolecular approach to preparation of polymer blends with tunable properties (thermal, mechanical and dynamic mechanical) was attributed to the presence of UPy associating groups that improve the compatibility between homopolymers with entirely different backbones. It was shown that improved interface adhesion caused a significant decrease in phase domain of the binary polymer blend and that the mechanical properties changed consequently. Network formation between PTHF2900 $(UPy)_2$ and a trifunctional polycaprolactone through thermoreversible crosslinks has the advantage of ease of processing while is expected to produce materials with desirable mechanical properties. Therefore, a supramolecular polymer with three UPy end groups, PCL900$(UPy)_3$ was prepared. PTHF2900$(UPy)_2$ was blended with

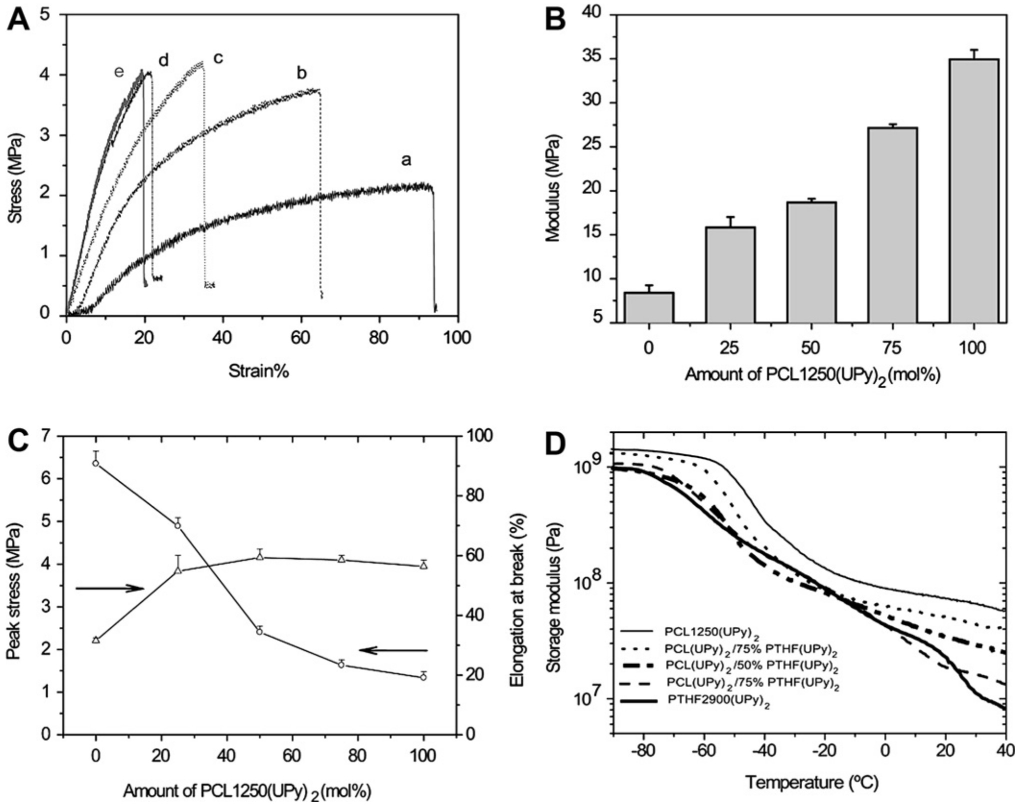

**Fig. 4.** Mechanical and dynamic mechanical properties of the supramolecular polymers and their blends; A: Tensile testing of supramolecular polymer/polymer blends. The stress is plotted against the strain for the neat polymers and their blends as indicated in the figure, a: PTHF2900(UPy)$_2$, b: PTHF(UPy)$_2$/25% PCL(UPy)$_2$, c: PTHF(UPy)$_2$/50% PCL(UPy)$_2$, d: PTHF(UPy)$_2$/75% PCL(UPy)$_2$ and e: PCL1250(UPy)$_2$. B and C: Variation of the Young's modulus (B) and elongation at break (C) with the blend composition. D: DMTA curves of PCL1250(UPy)$_2$, PTHF2900(UPy)$_2$ and their blends. Yielding is not observed for the blends with 50 and 75% PCL(UPy)$_2$ below 40 °C. The blend PTHF2900(UPy)$_2$/75% PCL1250(UPy)$_2$ demonstrates the highest storage modulus at room temperature.

different amounts of this trifunctional polycaprolactone (Fig. 5). Material properties of the blends were investigated with FT-IR, DSC and dynamic mechanical analysis and as a function of the PCL900(UPy)$_3$ content.

*3.2.2.1. Thermal properties.* Thermal properties of the neat PCL900(UPy)$_3$ and PTHF2900(UPy)$_2$ as well as their blends were studied with DSC and the results are summarized in Table 2. As it can be seen in the table, the glass transition temperatures of PCL900(UPy)$_3$ and PTHF2900(UPy)$_2$ demonstrate a slight shift in their position with the blend composition. All the three copolymers show two composition dependent glass transition temperatures. The corresponding glass transition of the PTHF2900(UPy)$_2$ component in the blends increased with increasing amount of PCL900(UPy)$_3$ as an indication of reversible crosslinking and therefore, decreased chain mobility. Restricted chain mobility is also evidenced by a continuous decrease in the heat capacity as the amount of the trifunctional polycaprolactone increased in the blends.

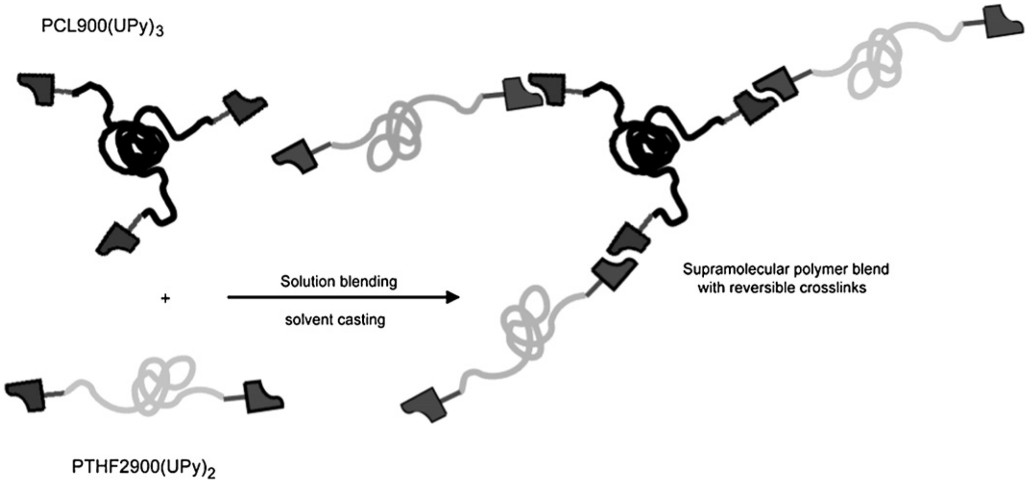

**Fig. 5.** Schematic display of blend preparation from PTHF2900(UPy)$_2$ and trifunctional PCL900(UPy)$_3$. Blends were prepared by solution mixing of homopolymers using chloroform as solvent.

**Table 2**
Glass transition temperatures, heat capacities, melting points and, heat of fusion of the supramolecular polymers/physically crosslinked blends.

| Polymer | $T_g$ (°C)[a] | ΔCp J/g.K | $T_m$ (°C) | $\Delta H_m$[b] J/g |
|---|---|---|---|---|
| PTHF2900(UPy)$_2$ | −78.8 | 1.58 | 23.8 | 45.5 |
| PTHF(UPy)$_2$/25% PCL(UPy)$_3$ | −78.3, −29.8 | 0.06,0.31 | 27.7, 91.8 | 18.21,6.60 |
| PTHF(UPy)$_2$/50% PCL(UPy)$_3$ | −76.4,−28.8 | 0.05,0.23 | 28.1, 93.2 | 10.94,6.60 |
| PTHF(UPy)$_2$/75% PCL(UPy)$_3$ | −74.8,−27.2 | 0.02,0.11 | 25.8,94.4 | 7.10,9.24 |
| PCL900(UPy)$_3$ | −22.5 | 0.14 | 93.3 | 11.10 |

DSC data was taken from the second heating run.

[a] $T_g$ was measured as the onset of the specific heat changes in the DSC trace.

[b] Total for two peaks.

*3.2.2.2. Mechanical properties.* Improved mechanical properties have been reported for low molecular weight polymers functionalized with strongly associating UPy groups [20,38]. The mechanical properties of (physically crosslinked) supramolecular polymer blends were studied with tensile testing and compared with those of the homopolymers. The representative stress-strain curves are displayed in Fig. 6. The supramolecular homopolymers represent completely different mechanical properties. PCL900(UPy)$_3$ is characterized with Young's modulus and stress at peak (tensile strength) of 126 and 13.8 MPa accompanied by a relatively small elongation at break of about 18%. Modulus and strength of the UPy functionalized polyether increased remarkably upon addition of PCL900(UPy)$_3$ and elongation at break decreased gradually at the same time. Shifting the copolymer component ratio of PTHF2900

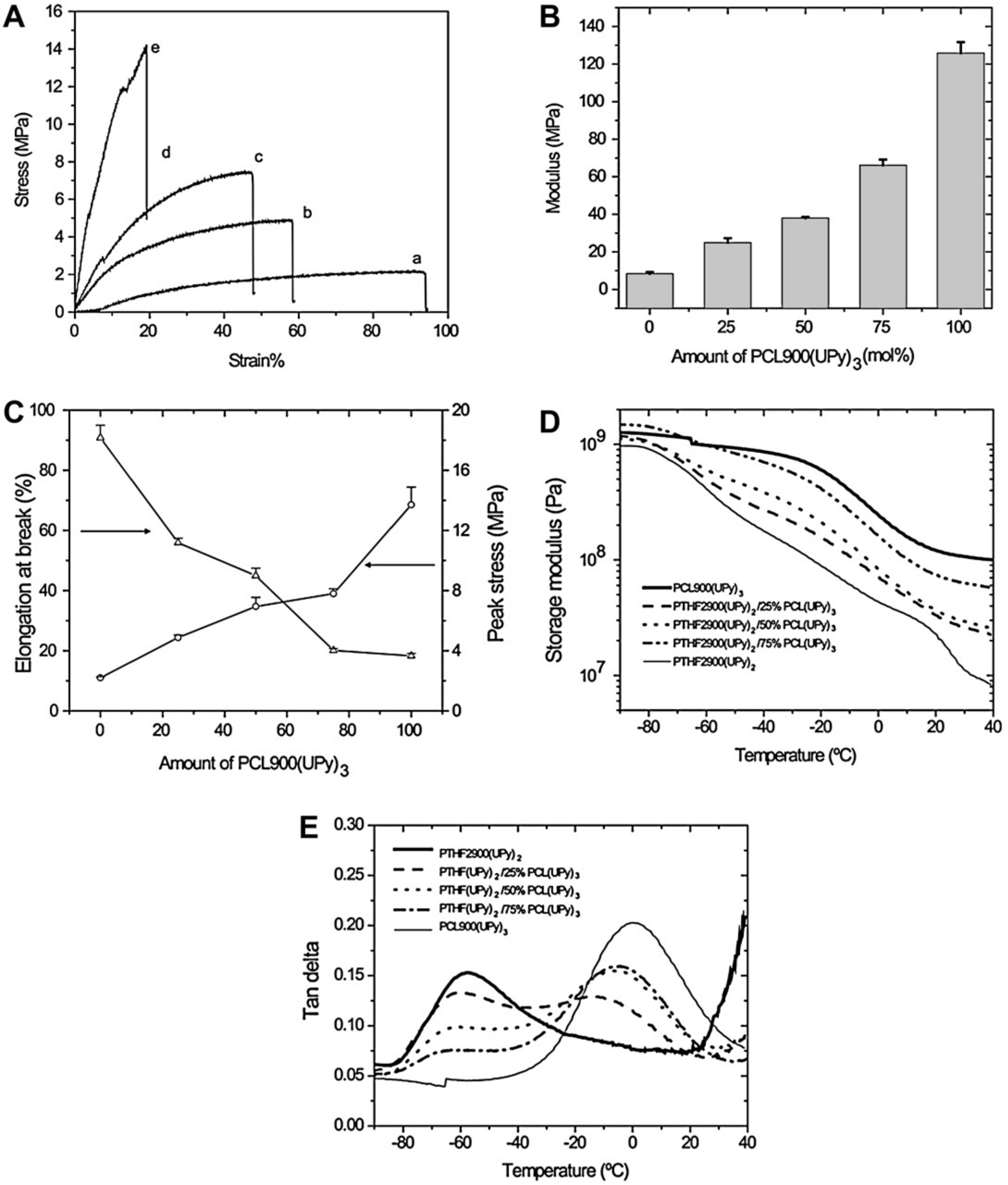

**Fig. 6.** A: Representative stress–strain curves of the pure polymers and their blends, a: PTHF2900(UPy)$_2$, b: PTHF(UPy)$_2$/25% PCL(UPy)$_3$, c: PTHF(UPy)$_2$/50% PCL(UPy)$_3$, d: PTHF (UPy)$_2$/75% PCL(UPy)$_3$ and e: PCL900(UPy)$_3$. B and C: Mechanical properties of PTHF2900(UPy)$_2$ and PCL900(UPy)$_3$ and the supramolecular blends their from. Variation of the Young's modulus (B), peak stress and elongation at break (C) with the concentration of PCL900(UPy)$_3$. D and E: Dynamic mechanical thermal properties of PTHF2900(UPy)$_2$/PCL900 (UPy)$_3$ copolymers; the effect of supramolecular blends preparation on D: storage modulus and E: tan delta.

$(UPy)_2$:PCL900$(UPy)_3$ from 100:0 to 50:50 resulted in significantly stiffer (modulus increased almost 5-fold) and stronger (tensile strength) material; more and more force is required to pull-out the polymer chains from the physically crosslinked blend systems. Stiffness and strength of the copolymer PTHF2900$(UPy)_2$/75% PCL900$(UPy)_3$ were improved even more, however, the material demonstrated similar elongation to the trifunctional homopolymer (Fig. 6).

*3.2.2.3. Dynamic mechanical thermal analysis.* Variations in the storage modulus and the damping factor of the homopolymers and their blends with temperature are displayed in Fig. 6. Two distinct glass transitions (values agree with those from DSC measurements) appeared for copolymers of PTHF2900$(UPy)_2$ and PCL900$(UPy)_3$. The dynamic mechanical behavior of PTHF2900$(UPy)_2$/25% PCL900 $(UPy)_3$ between −100 and 40 °C is characterized by changes in the storage modulus, showing a sudden and pronounced drop above the first glass transition (at about −78 °C). At the temperature region between this point and the corresponding glass transition of PCL900$(UPy)_3$ (about −30 °C) a relatively high modulus (about 0.28 GPa) area is observed indicating that the chain motions of PTHF2900$(UPy)_2$ are restricted by the network of PCL900$(UPy)_3$ which is still in the glassy state. The storage modulus dropped again at the glass transition of PCL900$(UPy)_3$ and reached about 30 MPa at room temperature. Similar behavior was observed for PTHF2900 $(UPy)_2$/50% PCL900$(UPy)_3$ except that a more steady region with remarkably higher modulus (about 0.44 GPa) was developed between corresponding glass transitions of the individual homopolymers. Storage modulus decreased after the second glass transition for this sample, to a value of 34 MPa at room temperature. Two glass transitions (at about −74 and −27 °C) were observed for PTHF2900$(UPy)_2$/75% PCL900$(UPy)_3$, with an area of significantly higher modulus (about 0.77 GPa) between the two transitions. Storage modulus is more temperature dependent in the region between the two glass transitions for the blends PTHF2900$(UPy)_2$/ 25% PCL900$(UPy)_3$ and PTHF2900$(UPy)_2$/75% PCL900$(UPy)_3$ as compared to PTHF2900$(UPy)_2$/50% PCL900$(UPy)_3$ suggesting a larger interfacial area and finer phase morphology [39].

Inspection of the storage modulus curves showed that PTHF2900$(UPy)_2$ starts to yield at temperatures above 20 °C while all the blends retain their stiffness and no sign of yielding was observed upon heating up to 40 °C. This is of special importance from a practical viewpoint, because addition of small quantities of a trifunctional supramolecular polymer appears to be enough to enlarge the working temperature range of a soft and flexible supramolecular polymer of very low melting temperature. The $\tan\delta$ peak intensity of PCL900$(UPy)_3$ decreased continuously (Fig. 6E) upon addition of increasing amounts of PTHF2900$(UPy)_2$ suggesting that less energy was dissipated as heat in the copolymer system. Decreased energy dissipation is a direct result of smaller free volume and restricted molecular motions at $T_g$.

## 4. Conclusion

We showed here that new materials with tunable properties can be prepared from supramolecular polymers that were suitably functionalized with strongly self associating UPy end groups. In this effort, two different strategies were implemented. Firstly, a telechelic polytetrahydrofuran diol and a telechelic polycaprolactone diol were functionalized with UPy groups at both ends. Then, varying amounts of the supramolecular polyester were added to the polyether to yield so-called segmented copolymers with composition dependent mechanical properties. Our results showed that the mechanical properties of all the blends stand higher than those predicted from the rule of mixtures. This approach is impacted by the strong and directional UPy–UPy interaction at the interface and phase separation between the telechelic polymer chains (the soft segments) and the stacked UPy–UPy dimers (hard segments). Secondly, telechelic polycaprolactone triol was functionalized with UPy groups and different amounts of this trifunctional supramolecular polyester were added to the bifunctional PTHF$(UPy)_2$. The synergistic effect of phase compatibilization through UPy–UPy interactions and reversible crosslinking caused a remarkable increase in mechanical and dynamic mechanical properties. Strength at peak and elastic modulus of the blend with 50 mol% (equal to only 28 wt%) PCL900$(UPy)_3$ was enhanced drastically (3.1 and 4.8 times) compared to the neat PTHF$(UPy)_2$. The material still demonstrated a high elongation at break of about 45%. The resulting robust copolymers provide a large range of working temperatures as evidenced by DMTA measurements. Small error margins on the mechanical properties of all the blends reported here show that UPy functional groups behave effectively and the blends are homogeneous mixtures of the components. Versatile performance of supramolecular polycaprolactone in biomedical applications has been studied and reported before [40]. We also showed that the supramolecular polymer blending is a powerful tool to decrease the phase domains from micro- down to nano scale. This is particularly important in applications such as tissue engineering where substrates need to be homogeneous at nano scale (below the living cells size).

The results presented here show that the mechanical properties of the supramolecular polymer blends can be tailored over a wide range through simply mixing of the supramolecular polymers with appropriate functionalities and at explicit compositions. The enhanced mechanical properties of the physically crosslinked blends compared to the individual homopolymers shows that the reversible crosslinks in blends behave like entanglements in conventional covalent polymers. In contrast to the conventional crosslinked polymers where the network is in kinetic equilibrium, these reversibly crosslinked networks are in thermodynamic equilibrium. Hence, the supramolecular polymer networks can be easily processed into desired shapes while offering excellent mechanical properties at room temperature.

## Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2010.10.039.

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