6340 *Macromolecules* **2007,** *40,* 6340−6348

Supramolecular Copolyesters with Tunable Properties

D. J. M. van Beek, Martijn A. J. Gillissen, Bart A. C. van As, Anja R. A. Palmans, and Rint P. Sijbesma*

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

Received March 11, 2007; Revised Manuscript Received June 15, 2007

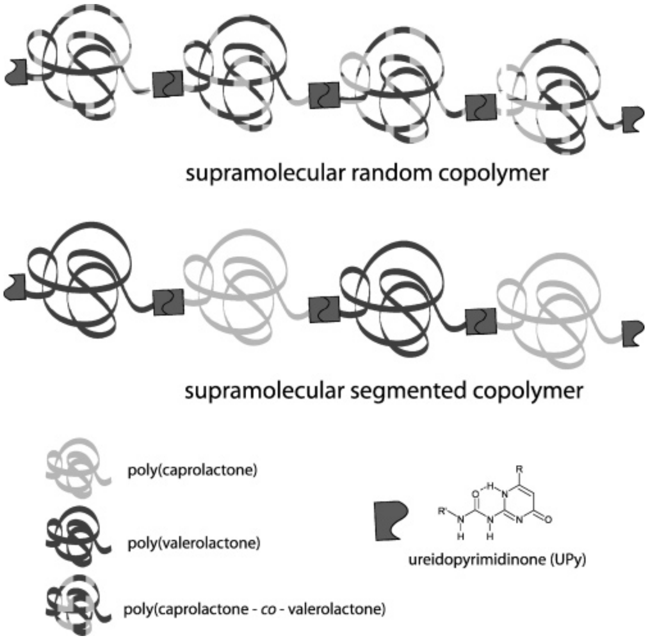
ABSTRACT: The effect of chain structure (supramolecular random copolymer vs supramolecular segmented copolymer) on material properties of supramolecular polymers was studied, using polyesters, end-functionalized with quadruple hydrogen-bonding ureidopyrimidinone (UPy) units. Mixing of miscible UPy homopolymers led to supramolecular segmented copolymers while functionalized random copolymer diols resulted in supramolecular random copolymers. The (co)polymers were prepared by (co)polymerization of ϵ-CL and δ-VL using Novozym 435, followed by end functionalization with UPy. Thermal analysis of the functionalized (co)polymers showed two melting transitions. With variable temperature IR, the lower transition was attributed to the melting of the polyester part, while the higher transition corresponded to melting of UPy moieties. The materials can therefore be considered as supramolecular thermoplastic elastomers with a hard phase of microphase separated UPy dimers, giving mechanical strength to the material. Mixing of UPy functionalized homopolymers gave better control over the mechanical properties than UPy functionalized copolymers as a correlation was found between the Young modulus and the fraction of δ-VL polymer in the material.

Introduction

Polyesters are commonly used in biomaterials because of their biocompatibility, biodegradability and tunable mechanical properties.[1−4] Poly(ϵ-caprolactone) (PCL)[4] is a particularly well studied aliphatic polyester receiving much attention due to its potential use in biomedical and pharmaceutical applications. However, due to its high crystallinity,[5] PCL degrades slowly,[2−4,6] which is a major drawback for a successful application as a biomaterial. Copolymerization[1,4,7] of ϵ-caprolactone (CL) with other monomers, as well as blending[8−13] with other polymers substantially improved the degradation rates. For example, copolymers of CL with ethylene glycol,[4,14] D- and L-lactide,[4,10] ω-pentadecalactone,[15,16] 1,5-dioxepan-2-one,[4,5] 1,4-dioxepan-2-one,[17] or δ-valerolactone[7,18−20] all showed enhanced hydrolysis rates due to a lower crystallinity in the copolymer. Moreover, the thermal and mechanical properties of the copolymers could be tuned by varying the copolymer composition.[19] However, if small modifications of the copolymer are required such as a different comonomer ratio or the incorporation of a slightly more polar monomer, the complete polymerization procedure needs to be repeated. Moreover, minor chemical modifications may require a radical change of the synthetic procedure such as the need of protection and deprotection steps. Here, we report a method based on reversible supramolecular interactions, which allows for a simple modification of the copolymer without the need of elaborate synthesis.

Supramolecular polymerizations based on quadruple hydrogen bonding of the ureidopyrimidinone (UPy) moiety (Scheme 1) was developed and elaborately studied in our laboratory.[21,22] Upon end-functionalization with the UPy moiety of low molecular weight polymers with low tensile strength, the macromonomers polymerize via hydrogen bonding to form elastic materials with useful mechanical properties.[22−24] Dramatic changes in mechanical properties were found for a wide range of polymers such as polyethers, polycarbonates and polyesters. Microphase separation between the UPy moiety and the polymer backbone was shown to contribute significantly to the improvement of mechanical properties in, e.g., UPy functionalized poly(ethylene butylene).[22,25,26] Supramolecular polymerization allows the formation of segmented copolymers, which has been reported for non-miscible diblock copolymers[27−29] and non-miscible segmented copolymers.[28,30−33] In this paper, we will focus on the preparation of miscible segmented copolymers by simply mixing of functionalized homopolymers.[24]

Scheme 1. Supramolecular Random Copolymers (First Copolymerize, Then Functionalize) and Supramolecular Segmented Copolymers (Mixing of Homopolymers)



Two methods of preparation of supramolecular copolymers as depicted in Scheme 1 are compared in this study. First, low molecular weight random copolymers are discussed, which after functionalization with UPy moieties result in supramolecular

---

* Corresponding author. E-mail: r.p.sijbesma@tue.nl.

10.1021/ma0705927 CCC: $37.00

random copolymers. These are compared with supramolecular segmented copolymers, which are obtained by mixing of functionalized homopolymers. Homo- and copolymers of ϵ-caprolactone (CL) and δ-valerolactone (VL) were selected to prepare the supramolecular copolymers because of vast knowledge of their chemical structure and thermal properties and their potential as biomaterials.[4,7,18−20] Ring-opening polymerizations of lactones can be performed chemically[4,34−36] or enzymatically.[37−40] All polymerizations presented here were performed enzymatically, using the immobilized Lipase B from *Candida antarctica* (Novozym 435) as it is then possible to work under mild conditions. Moreover, it is known that the copolymerization of two lactones using Novozym 435 results in random copolymers.[16,41−43] In the present work, the possibility to tune both thermal and mechanical properties of copolymers by using supramolecular chemistry is investigated, and the method which leads to materials with the best tunable material properties is identified.

Experimental Section

Chemicals. ϵ-Caprolactone was used as received from Fluka; δ-valerolactone (Fluka) was distilled prior to use. 2(6-Isocyanatohexylaminocarbonylamino)-6-methyl-4[1*H*]pyrimidinone (UPy-NCO) was synthesized as reported.[23] Novozym 435 was obtained from Novozymes A/S. Toluene was freshly distilled from sodium prior to use. Bis(triphenylphosphine)nickel(II) bromide and 1,6-hexanediol were both obtained from Acros. The aminomethyl polystyrene resin (200−400 mesh) was obtained from Nova Biochem. All chemicals were used without further purification unless stated otherwise.

Analytical Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 200, Varian Gemini 300, or Varian Mercury 400 in deuterated chloroform, chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and the delay time (d_1) was set to 10 s. Gel permeation chromatography (GPC) was carried out on a Waters 712 WISP HPLC system with Waters 410 Differential refractometer detector and a PL gel guard precolumn (5 mm, 50 × 7.5 mm) followed by two PL gel mixed-C columns (10 mm, 300 × 7.5 mm, Polymer Laboratories), using THF as the eluent. Sample concentrations were 1 mg/mL in THF, and all molecular weights were relative to polystyrene standards.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 with DSC Autosampler and Perkin-Elmer CCA7 cooling element under a nitrogen atmosphere. The melting temperatures (T_m) with corresponding transition enthalpies (ΔH) were determined from the second heating run (10 K/min), while the glass transition temperature was determined at a scan speed of 40 K/min (third heating run) on samples of 8−12 mg.

Determination of CL/VL Ratio in Prepolymer Diols. The integrated peak areas of the signals at δ = 1.44 ppm (A), with contributions of CL (n) and initiator (x), and those at δ = 2.37 ppm (B), with contributions of VL (m), CL, and initiator, were used to calculate the CL/VL ratio in the prepolymer diols by solving eqs 1 and 2. From the integrated peak area of C**H**$_2$OH (δ = 3.67 ppm) the contribution of 1 CH$_2$ (x) to the integrated peak area was calculated (divide the integrated peak by 2 as there are two end groups in each chain contributing to the integrated peak area).

$$A = 2n + 3x \qquad (1)$$

$$B = 2m + 2n + 2x \qquad (2)$$

Variable Temperature Infrared Spectroscopy. Attenuated total reflection infrared (ATR-IR) spectroscopy was measured on small polymer films using a BioRad Excalibur 3000 spectrometer equipped with a Specac Golden Gate ATR setup. The IR spectra were recorded over a spectral range of 650 up to 4000 cm^{-1} with a resolution of 4 cm^{-1} coadding 8 scans. For temperature calibration of the IR measurements, benzil (Reichert, Vienna, T_m = 95 °C), phenyl ether (Fluka, T_m = 27 °C), biphenyl (Across, T_m = 68 °C) and benzoic acid (Merck, T_m = 122 °C) were used as reference compounds.

Tensile Testing. Films were prepared by dissolving the polymers (total of 1.5 g) in chloroform (15 mL) and drop casting these solutions in Teflon dishes of 105 × 45 × 5 mm. The dishes were covered with a beaker to allow the solvent to evaporate slowly. After solvent evaporation, the films were dried for a minimum of 10 h at 30 °C in vacuum and were stored at room temperature for at least a week. Tensile bars (according to ASTM D1708−96 dimensions) were punched from these films. Tensile properties were measured according to ASTM D1708-96 in air at room temperature. The thickness of the samples was always very close to 0.3 mm. Testing was conducted in a Zwick Z010 Universal Tensile Tester equipped with a 20 N load cell. The crosshead speed was 2.2 mm/min with an initial length of 22 mm and 5 samples were evaluated to determine Young's modulus and stress and strain at break. An indicative Young's modulus was determined using eq 3, where σ_1 is the stress at a strain (ϵ_1) of 0.0005 and σ_2 is the stress at a strain (ϵ_2) of 0.0025.

$$E_I = (\sigma_2 - \sigma_1)/(\epsilon_2 - \epsilon_1) \qquad (3)$$

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMTA) tests were performed on films drop cast from chloroform in a Teflon dish covered with a beaker to allow slow evaporation of chloroform. The films were then dried for at least 8 h in a vacuum oven at 30 °C and were evaluated within 2 days after preparation. DMTA was performed on a TA Instruments Q800 Dynamic analyzer in film tension mode to determine the dynamic modulus (E_d) and the tangent of the phase lag (tan δ). Samples were characterized at 1 Hz during a temperature ramp of 2 °C/min starting at −80 °C (to determine the mechanical glass transition temperature) up to the temperature limit at which the elastic modulus was experimentally inaccessible. The thickness of the films was always close to 0.2 mm and a length of more than 20 mm, the width was always 5.3 mm controlled by the size of the punch used to cut the samples.

General Procedure of Ring-Opening Polymerization of Lactones Catalyzed by Novozym 435: High Molecular Weight Polymers. Prior to all ring-opening polymerizations, Novozym 435 was dried over P$_2$O$_5$ at 1 mbar for 24 h.[37] To obtain high molecular weight polymers, a lactone solution (2 M in toluene with 4 Å molecular sieves) with Novozym 435 (2.5 mg/mmol lactone) was stirred at 40 °C under an argon atmosphere. The water present in the enzyme was used as initiator. The conversion of the lactone was followed with ^{1}H NMR and when the conversion was >90%, bis(triphenylphosphine)nickel(II) bromide was added to inhibit the enzyme and the reaction mixture was filtered over a glass filter to remove the enzyme.[44] Polymers were precipitated from chloroform in methanol.

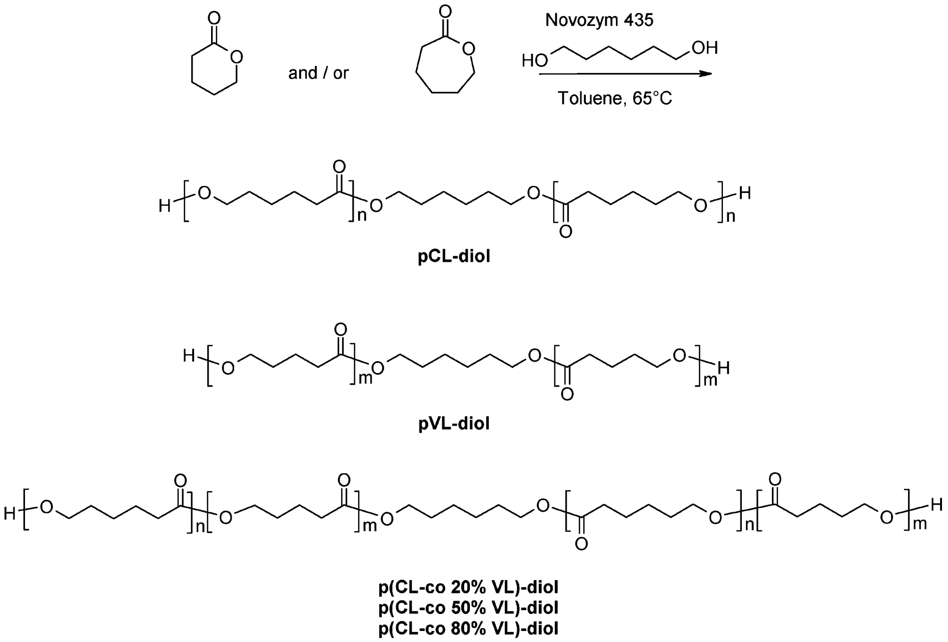
pCL (Entry 1). The reaction was stopped after 6 days. The polymer was precipitated from chloroform in methanol and a white powder was obtained. Yield: 34%. GPC (THF): M_n = 82.6 kg/mol, PDI = 2.0.

pVL (Entry 2). The reaction was stopped after 19 days. After precipitation from chloroform in heptane, the polymer was obtained as a white powder. Yield: 50%. GPC (THF): M_n = 22.3 kg/mol, PDI = 6.3.

p(VL-*co*-CL) (Entry 3). The reaction was stopped after 11 days. The product was precipitated from chloroform in heptane and oil was obtained. Yield: 66%. GPC (THF): M_n = 6.9 kg/mol, PDI = 4.3.

General Procedure of Ring-Opening Polymerization of Lactones Catalyzed by Novozym 435: Prepolymer Diols. The reaction mixture was prepared by adding the appropriate lactone, 1,6-hexanediol and freshly distilled toluene (~2 M mixture of lactone in toluene) into a dry flask with stirring bar. Copolymers were obtained by mixing of CL and VL in different ratios. The reaction was started by addition of the dried Novozym 435 to the mixture and increasing the temperature to 65 °C. After reaching a

Scheme 2. Ring-Opening Polymerization of Lactones Catalyzed by Novozyme 435



conversion over 90% (checked by ^{1}H NMR), the enzyme was filtered off over a P4 glass filter and solvent was evaporated under reduced pressure. All polymers were precipitated in *n*-heptane to remove the unreacted monomer. The resulting white powders or oils were isolated, dried and characterized using ^{1}H NMR, ^{13}C NMR, GPC, and DSC.

pCL-diol (Entry 4): Waxy solid. Yield: 94%. GPC (THF): $M_n = 3.4$ kg/mol, PDI = 1.5.

pVL-diol (Entry 6): Waxy solid. Yield: 74%. GPC (THF): $M_n = 2.3$ kg/mol, PD = 1.8.

p(CL-*co* 20% VL)-diol (Entry 8): Oil. Yield: 96%. GPC (THF): $M_n = 2.9$ kg/mol, PDI = 1.8.

p(CL-*co* 33% VL)-diol (Entry 10): Oil. Yield: 86%. GPC (THF): $M_n = 2.9$ kg/mol, PDI = 1.7.

p(CL-*co* 80% VL)-diol (Entry 12): Oil. Yield: 98%. GPC (THF): $M_n = 3.0$ kg/mol, PDI = 1.5.

General Procedure for the Reaction of Prepolymer Diols with UPy—Isocyanate. Hydroxyl end-terminated polymers were functionalized with UPy moieties according to a literature procedure.[23] The crude polymers were precipitated in heptane and isolated. The resulting elastic materials were dried at 25 °C in vacuum and characterized using ^{1}H NMR, ^{13}C NMR, GPC, and DSC.

pCLdiUPy (Entry 5). Yield: 60%. GPC (THF): $M_n = 3.8$ kg/mol, PDI = 1.6.

pVLdiUPy (Entry 7). Yield: 77%. GPC (THF): $M_n = 3.0$ kg/mol, PDI = 1.7.

p(CL-*co* 14% VL)diUPy (Entry 9). Yield: 45%. GPC (THF): $M_n = 4.6$ kg/mol, PDI = 1.5.

p(CL-*co* 33% VL)diUPy (Entry 11). Yield: 79%. GPC (THF): $M_n = 2.7$ kg/mol, PDI = 1.8.

p(CL-*co* 80% VL)diUPy (Entry 13). Yield: 34%. GPC (THF): $M_n = 8.9$ kg/mol, PDI = 1.3.

Results and Discussion

Synthesis of High Molecular Weight pCL, pVL, and p(CL-*co* 50% VL). High molecular weight polyesters (**pCL**, **pVL**, and **p(CL-*co* 50% VL)**) were synthesized as reference materials to compare the thermal and mechanical properties of supramolecular (co)polymers with "traditional" polymers. The polyesters were obtained by enzymatic ring-opening polymerization of the corresponding lactones employing Novozym 435 as the catalyst. To reduce the amount of water, which acts as initiator and limits the molecular weight, all reagents and Novozym 435 were rigorously dried as previously described.[37] Although the drying procedure significantly slows down the reaction rate, polyesters of good molecular weight are accessible in this way.[40] For example, **pCL** was obtained with a M_n of 82.6 kg/mol and a PD of 2.0 with a reaction time of 6 days. In contrast to **pCL** and **pVL**, which were white powders, **p(CL-*co* 50% VL)** was obtained as an oil.

Table 1. Feed Ratio and Observed Molar Ratio of CL (*n*) and VL (*m*) in Random Copolymers before and after Functionalization with the UPy Moiety Obtained from ^{1}H NMR

random copolymer	molar feed ratio CL/VL (*n*:*m*)	observed molar ratio CL/VL (*n*:*m*)
p(CL-*co* 20% VL)diol	80:20	81:19
p(CL-*co* 14% VL)diUPy	81:19	86:14
p(CL-*co* 50% VL)diol	50:50	52:48
p(CL-*co* 33% VL)diUPy	52:48	67:33
p(CL-*co* 80% VL)diol	20:80	18:82
p(CL-*co* 80% VL)diUPy	18:82	20:80

Synthesis of Supramolecular (Co)Polymers. Low molecular weight prepolymers, poly(caprolactone diol) (**pCL-diol**), poly(valerolactone diol) (**pVL-diol**), and random copolymers of CL and VL with varying VL content (entries 8, 10, 12), were obtained by modification of the method to obtain high molecular weight polyesters (Scheme 2). A bifunctional initiator, 1,6-hexanediol, was used in a 1:20 I/M ratio, ensuring that all polymer chains have two diol end groups.

Using this procedure, polymer diols with a M_n of approximately 2 kg/mol were obtained as determined by NMR and GPC. From ^{1}H NMR, the ratio of CL (n) to VL (m) was determined by comparison of the integrated peak areas of the signals at $\delta = 1.44$ ppm and $\delta = 2.37$ ppm (See Experimental Section). The observed and feed ratios are in good agreement for all polymer diols (Table 1).

All prepolymers were subsequently functionalized with the ureidopyrimidinone (UPy) group by reaction with the UPy−NCO synthon (Scheme 3) according to the literature procedure.[23] In the preparation of **p(CL-*co* 33% VL)diUPy**, the excess of UPy−NCO was removed by reaction with a aminomethyl polystyrene resin after which precipitation in heptane followed. Table 1 summarizes the CL/VL ratio in the UPy functionalized polymers after workup. For both **p(CL-*co* 14% VL)diUPy** and

Scheme 3. Functionalized Supramolecular (Co)Polymers

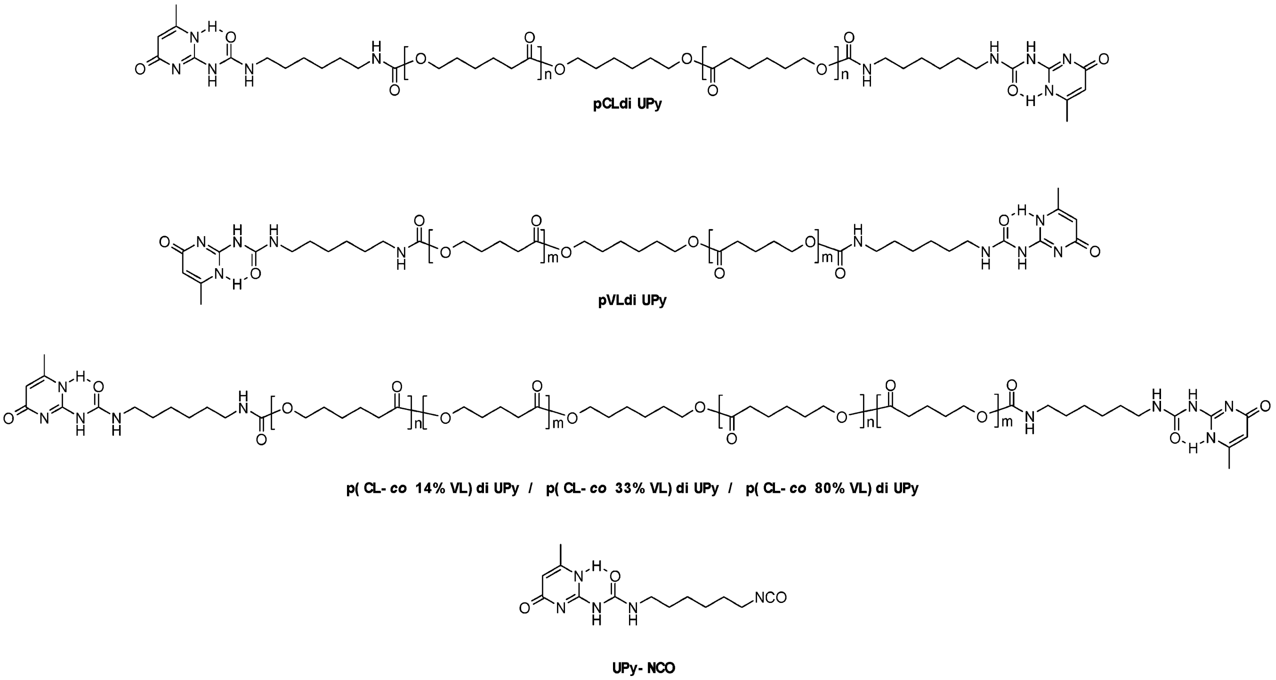


Table 2. Composition, Molecular Weight and Thermal Properties of HMW (Co)Polymers, (Co)Polymer Diols, Supramolecular (Co)Polymers, and Mixtures of Supramolecular Polymers

entry	polymer	CL [%]	VL [%]	yield [%]	M_n[c] [kg/mol]	PDI[c]	T_g [°C]	T_m [°C]	Δ*H* [J/g]
1	**pCL**	100	0	34	82.6	2.0	−58	53	62
2	**pVL**	0	100	50	22.3	6.3	−50	55	61
3	**p(VL-*co*-CL)**	50	50	66	6.9	4.3	−60	15	64
4	**pCL-diol**	100	0	94	3.4	1.5	−63	46	95
5	**pCLdiUPy**	100	0	60	3.8	1.6	−55	39/63	32[a]
6	**pVL-diol**	0	100	74	2.3	1.8	−61	42	75
7	**pVLdiUPy**	0	100	77	3.0	1.7	−50	34/77	8/8
8	**p(CL-*co* 20% VL)-diol**	81	19	96	2.9	1.5	−62	28/33	57[a]
9	**p(CL-*co* 14% VL)diUPy**	86	14	45	4.6	1.5	−55	22/52	24/6
10	**p(CL-*co* 50% VL)-diol**	50	50	86	2.9	1.7	−88[b]	6	53
11	**p(CL-*co* 33% VL)diUPy**	67	33	79	2.7	1.8	−56	73	6
12	**p(CL-*co* 80% VL)-diol**	18	82	98	3.0	1.5	−84	13	48
13	**p(CL-*co* 80% VL)diUPy**	20	80	34	8.9	1.3	−49	23/34	49[a]
14	**Mix(pCLdiUPy/20% pVLdiUPy)**	80	20	n.a.	n.a.	n.a.	−55	38/65	21[a]
15	**Mix(pCLdiUPy/50% pVLdiUPy)**	50	50	n.a.	n.a.	n.a.	−54	30/70	13[a]
16	**Mix(pCLdiUPy/77% pVLdiUPy)**	23	77	n.a.	n.a.	n.a.	−52	34/74	15[a]

[a] Total for two transitions. [b] Determined from second heating run. [c] Determined by GPC in THF. n.a.: not applicable.

p(CL-*co* 80% VL)diUPy the CL/VL ratio slightly increased upon functionalization. For **p(CL-*co* 33% VL)diUPy**, on the other hand, the CL/VL ratio significantly and reproducibly increased from 50/50 to 67/33. Functionalization of the diols was performed in the presence of dibutyl tin dilaurate (DBTDL), which is a Lewis acid, which is known to depolymerize pVL segments.[19,45] In order to investigate the influence of DBTDL on copolymer composition samples of **pVL-diol**, **pCL-diol**, and **p(CL-*co* 50% VL)diol** were refluxed in chloroform with and without DBTDL for 72 h and monitored with GPC. Refluxing in the presence of DBTDL did not affect the composition of **pCL-diol**, while for **pVL-diol** and **p(CL-*co* 50% VL)diol**, a signal corresponding to VL monomer was observed after 16 h. In the absence of DBTDL, such a signal was not observed. (See Supporting Information for GPC data) Therefore, the shift in CL/VL ratio after functionalization with UPy moieties is attributed to the action of DBTDL. All supramolecular (co)-polymers (entries 5, 7, 9, 11, 13) (Scheme 3) were obtained in yields varying from 34 to 77%. (Table 2).

Thermal Properties. The thermal properties of the polymers were investigated using differential scanning calorimetry (DSC) and variable temperature attenuated total reflection infrared spectroscopy (ATR−IR). The melting temperatures around 55 °C and glass transitions at −60 °C observed for **pCL** (entry 1) and **pVL** (entry 2) (Figure 1A), are in good agreement with values previously reported in literature.[5,12,18,36] In the IR (Figure 1B), a shift from 1724 cm^{-1} (crystalline ν_s(C=O)) to 1737 cm^{-1} (amorphous ν_s(C=O)) was observed around 56 °C, indicating melting of PCL[12,13,46,47] and PVL.[12] The signal at 1724 cm^{-1} decreased for both polymers, while a new and much stronger signal appeared at 1737 cm^{-1}, represented in Figure 1B. Melting was furthermore confirmed by the disappearance of the stretch vibration at 1293 cm^{-1}, corresponding to the C−O and C−C stretch vibrations of the crystalline fraction of the material. (Figure 1B, inset) The thermal behavior of **p(CL-*co*-VL)** (entry 3) differs distinctly from the homopolymers **pCL** and **pVL** as the melting temperature is approximately 40 °C lower (Table 2, Figure 1A). A lowering in the melting temperature of

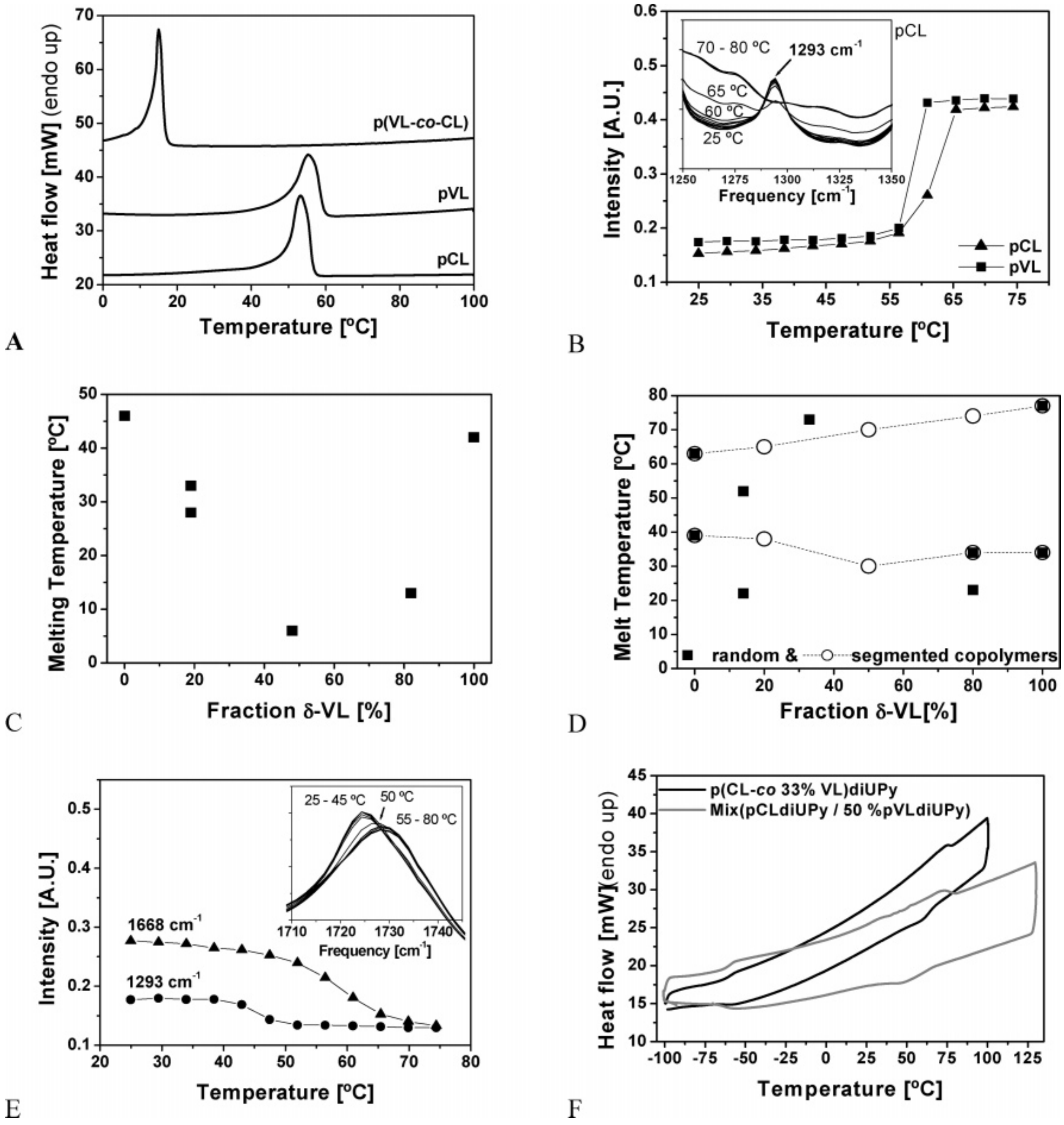


Figure 1. (A) DSC traces of **pCL**, **pVL**, and **p(VL-*co*-CL)**. (B) ATR−IR of **pCL** (triangles) and **pVL** (squares) at 1737 cm^{-1}. Inset: ATR−IR of **pCL** at 1293 cm^{-1}. (C) Melting temperatures of prepolymers diols vs δ-VL fraction. (D) Melting temperatures of supramolecular random copolymers (squares) and supramolecular segmented copolymers (circles) vs δ-VL fraction. (E) ATR−IR of **pCLdiUPy** vs temperature, inset: ATR−IR at 1724 cm^{-1}. (F) DSC traces of **p(CL-*co* 33% VL)diUPy** (black), **Mix(pCLdiUPy/50% pVLdiUPy)** (gray).

copolymers of VL and CL has been observed previously by Storey et al.[19] and Faÿ et al.[18] Furthermore, Gruvegård[5] and co-workers suggested that suppression of melting points observed for copolymers originates from a mismatch in the sequence length of the crystal. The conformations in the crystals of CL and VL are both planar zigzag, however, the sequence length of CL (17.0 Å) is slightly bigger than for VL (15.7 Å), a plausible reason for a suppressed melting point. The work of Furuhashi et al.[48] supports this latter work as they concluded that due to the odd number of methylene units in CL the carbonyl ester groups are distributed regularly on both sides of the chains, in contrary to even-numbered polymers like VL.

The homopolymers **pCL-diol** and **pVL-diol** display single melting points at 46 °C and 42 °C (Figure 1C), respectively. This is substantially below the melting temperatures found for **pCL** and **pVL** of 53 and 55 °C, respectively. The differences are attributed to the significantly lower molecular weights of **pCL-diol** and **pVL-diol**. Furthermore, the random copolymer diols (entries 8, 10, 12) also display single melting temperatures, indicating that no macrophase separation between VL and CL occurred. However, an additional melting point at 28 °C is observed for **p(CL-*co* 20% VL)-diol**, but the origin of this transition is not clear. The random copolymer diols all show lower melting temperatures than the corresponding homopolymer diols as a consequence of the random character of the copolymers (vide supra). Glass transition temperatures were observed below −60 °C for all prepolymer diols (Table 2).

All UPy functionalized materials showed similar glass transition temperatures around −55 °C, but significant differences in the melting points were observed (Table 2). Furthermore, the polymers changed from oils or waxy solids into elastic solids upon functionalization.[22,23] Besides **p(CL-*co* 33% VL)-diUPy**, all polymers functionalized with UPy moieties displayed two melting temperatures. (Table 2 and Figure 1D) Variable temperature IR was performed to investigate the nature of the melting temperatures in the supramolecular polymers. Figure 1E shows the infrared spectrum for **pCLdiUPy** as a function of temperature, which is representative for the other polymers.

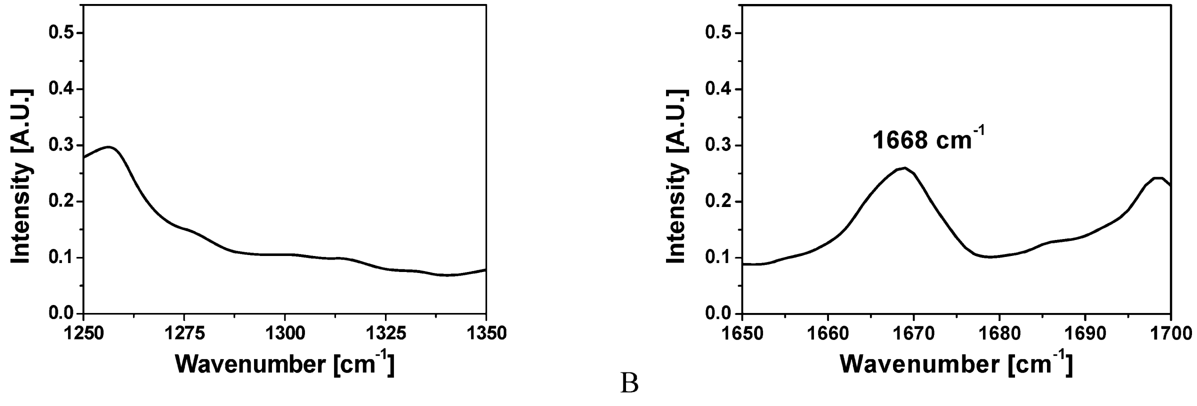


Figure 2. ATR−IR of **p(CL-*co* 33% VL)diUPy** at (A) 1293 and (B) 1668 cm^{-1}.

The intensities of the absorption bands at 1724, 1668, and 1293 cm^{-1} were evaluated as a function of temperature. The bands at 1724 and 1293 cm^{-1} are typical for the crystalline C═O vibration of polyesters and their intensities are expected to decrease when pCL and pVL become amorphous.[12,46,47] Around 45 °C a decrease in intensity at 1293 cm^{-1} and a shift from 1724 cm^{-1} to higher wave numbers were indeed observed (Figure 1E and inset), corresponding to the lowest melt transition at 39 °C. The band at 1668 cm^{-1} originates from the UPy moiety, although we cannot assign it to a specific vibration.[49,50] A closer look to the intensity at 1668 cm^{-1} showed a decrease around a temperature of 60 °C, corresponding to the highest melting transition at 63 °C. We conclude that the lowest melting temperatures can be attributed to the melting of the polyester backbone and the highest melting temperature can be attributed to melting of the UPy moiety. Therefore, microphase separation of the UPy moiety and polymer part is indeed the origin of the appearance of two melting peaks. Although functionalized with UPy moieties, the melting temperatures of the polyester backbone show a δ-VL fraction dependency, similar to the melting temperatures as observed for the (co)polymer diols (Figure 1C).

Unexpectedly, **p(CL-*co* 33% VL)diUPy** displayed only one melting temperature at 73 °C. Infrared spectroscopy at room temperature (Figure 2A) showed the absence of a vibrational band at 1293 cm^{-1}, indicating an amorphous polyester backbone at room temperature. This is in line with the maximum in melting point depression previously described by Storey[19] et al. for a CL/VL ratio of 67/33. The characteristic vibration corresponding to the crystalline form of the UPy moiety at 1668 cm^{-1} (Figure 2B) is present at room temperature. The melting point observed at 73 °C is therefore attributed to melting of microphase separated domains of UPy dimers. High melting points for UPy moieties have been observed before for polymers with an amorphous backbone. Thermal analysis of UPy telechelic (amorphous) poly(ethylene butylene)[25] showed a single melting transition at 69 °C in the first heating run, attributed to the melting of the microphase separated UPy moieties. The slight differences in melting temperature of the UPy moieties can be explained by the enhanced UPy crystallite formation in an amorphous polymer matrix due to higher mobility of the UPy groups, resulting in larger crystallites with a higher melting temperature.

The melting transitions corresponding to melting of the UPy moieties observed for the supramolecular random copolymers do not show any relation with increasing VL ratio (Figure 1D). Whereas melting point suppression is absent in the supramolecular segmented copolymers, higher values for the melting transitions of the polymer backbones (entries 14, 15, and 16) were observed, compared to the supramolecular random copolymers (Figure 1D). The presented supramolecular segmented copolymers show a constant melting temperature (34 °C) similar to the blended CL/VL oligomers studied by Storey.[19] In addition, a linear increase of the melting temperature of the UPy moiety from 63 to 77 °C with increasing VL content was observed.

Mechanical Properties. Functionalization of low molecular weight polymers with UPy groups leads to improved mechanical properties.[22,23] The mechanical properties of the copolymers were studied by tensile testing and representative stress−strain curves are depicted in Figure 3 whereas the results are summarized in Table 3. The mechanical properties of the pure polymers, **pCLdiUPy** and **pVLdiUPy**, represent the two extremes. **pCLdiUPy** is slightly more brittle (Table 3) but is more flexible than **pVLdiUPy** as indicated by Young's moduli of 28 and 45 MPa, respectively. As the maximum applied stress for **pCLdiUPy** (2.9 MPa) is lower than for **pVLdiUPy** (4.7 MPa), **pCLdiUPy** is also weaker. The supramolecular polymers differ in a similar manner from each other as the high molecular weight counter parts (entries 1 and 2). **pCL** is also more though, more flexible but weaker than **pVL** (Table 3). Although Young's modulus seems to increase with increasing VL content, no relation between the stress−strain curves and the ratio of VL to CL in the copolymers can be observed for the random copolymers (Figure 3A). Because of limited availability, **p(CL-*co* 80% VL)diUPy** was only measured once and its results cannot be interpreted with great certainty. All tensile tests were preformed at room temperature and when a closer look is taken to Figure 1D, it becomes clear that the polymer backbones of the supramolecular random copolymers are all molten at room temperature. Remarkably, despite the molten polymer backbone, the materials have sufficient mechanical properties to undergo mechanical testing. Even **p(CL-*co* 33% VL)diUPy** displays good mechanical properties. The polymer properties of the supramolecular random copolymers are not influenced anymore by the composition of the polyester backbone but the material properties are mainly determined by the UPy dimers. Microphase separation of the polymer backbone and the UPy hydrogen-bonding moieties (melting temperatures above 30 °C) results in an elastomeric network, responsible for the strength and flexibility of the materials.

In contrast to the stress−strain curves of the supramolecular random copolymers, the stress−strain curves of the supramolecular segmented copolymers were found to lie between the two extremes. Moreover, a correlation between the stress−strain curves and the ratio CL:VL was observed (Figure 3B). Shifting the ratio of CL:VL from 20:80 to 80:20 by increasing **pVLdiUPy**, leads to more brittle but stronger and stiffer materials (Figure 2B) as evidenced by the increasing Young's modulus

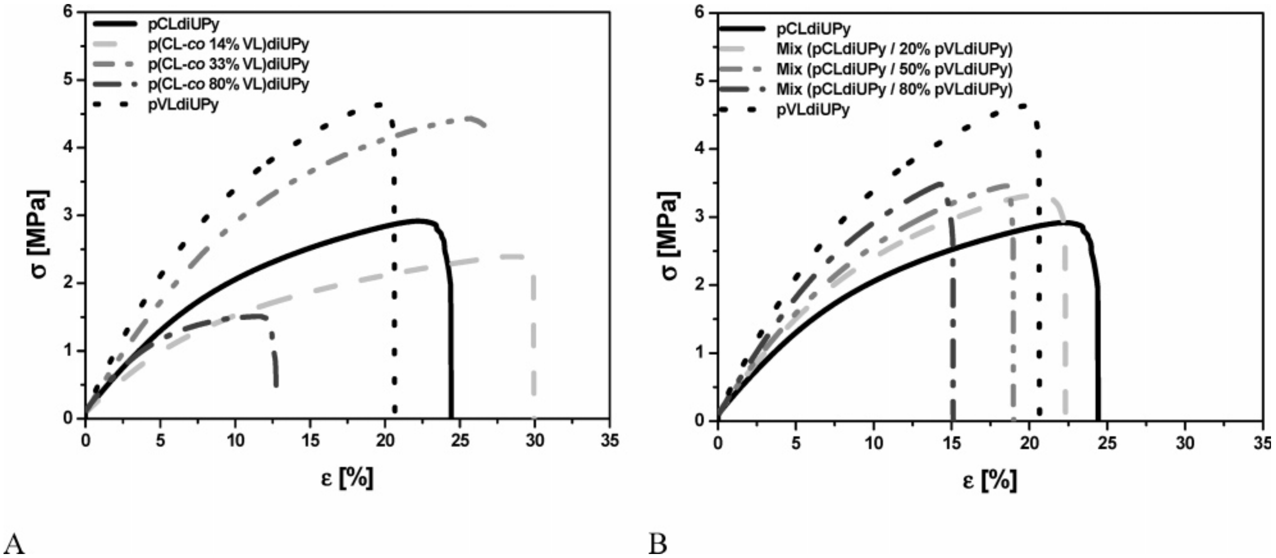


Figure 3. Representative stress−strain curves of (A) supramolecular random copolymers and (B) supramolecular segmented copolymers.

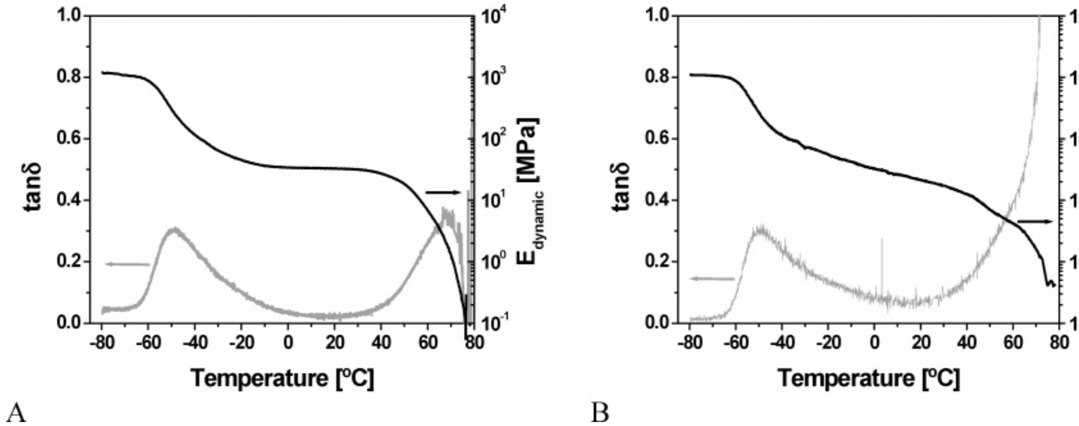


Figure 4. Dynamic mechanical analysis curves of (A) supramolecular random copolymer **p(CL-*co* 33% VL)diUPy** and (B) supramolecular segmented copolymer **Mix(pCLdiUPy/50% pVLdiUPy)**.

Table 3. Mechanical Properties of Supramolecular Random Copolymers and Supramolecular Segmented Copolymers with Data Derived from Engineering $\sigma-\epsilon$ Curves

polymer	E [MPa]	σ_{max} [MPa]	$\epsilon_{\mathbf{break}}$ [%]
pCLdiUPy	28.1 ± 0.6	2.9 ± 0.1	24.0 ± 1.9
pVLdiUPy	45.4 ± 1.2	4.7 ± 0.1	20.7 ± 1.1
p(CL-*co*-14% VL)diUPy	20.9 ± 0.5	2.4 ± 0.1	31.0 ± 1.4
p(CL- *co*-33% VL)diUPy	38.2 ± 4.2	4.4 ± 0.1	24.4 ± 1.2
p(CL- *co*-80% VL)diUPy[a]	29.0	1.5	12.8
Mix(pCLdiUPy/20% pVLdiUPy)	33.4 ± 0.5	3.4 ± 0.1	22.9 ± 1.1
Mix(pCLdiUPy/50% pVLdiUPy)	38.2 ± 4.2	4.4 ± 0.1	24.4 ± 1.2
Mix(pCLdiUPy/77% pVLdiUPy)	39.7 ± 2.5	3.8 ± 0.2	17.8 ± 1.7
pCL[b]	255 ± 25	15 ± 0.7	685 ± 112
pVL[b]	241 ± 158	22 ± 5.2	792 ± 163

[a] $n = 1$. [b] Representative stress−strain curves given in the Supporting Information.

(Table 3). Apparently, the polyester mainly present in the mixture, determines the material properties of the polymer film.

While tensile testing is performed at room temperature and allows for the determination of Young's modulus, dynamic mechanical thermal analysis (DMTA) permits us to investigate the mechanical properties from below the glass transition temperature up to the melting point. Comparison of the properties of materials with similar CL/VL ratios is of particular interest, and therefore DMTA was measured for **p(CL-*co* 33% VL)diUPy** and **Mix(pCLdiUPy/50% pVLdiUPy)**. Figure 4 depicts the dynamic moduli and tan δ of **p(CL-*co* 33% VL)diUPy** (Figure 4A) and **Mix(pCLdiUPy/50% pVLdiUPy)** (Figure 4B) against temperature.

For both polymers a gradual decrease in dynamic modulus ($E_{dynamic}$) is observed from glass to rubber and finally to melt. The dynamic moduli are very similar, indicating that below the glass transition temperature the polymers have similar properties. Both samples displayed a glass transition around −50 °C (maximum in tan δ), corresponding nicely to the glass temperatures found by DSC (Table 2). After the glass transition, a rubber plateau is reached for **p(CL-*co* 33% VL)diUPy** at a value of 40 MPa between −20 and 40 °C. The sample yielded around the melting temperature of the UPy moiety (73 °C). A higher value for the dynamic modulus is observed after the glass transition for **Mix(pCLdiUPy/50% pVLdiUPy)**. However, the dynamic modulus decreases with increasing temperature and no rubber plateau can be observed. Melting of the polymer backbone is visible by the drop in modulus around 40 °C. The sample of **Mix(pCLdiUPy/50% pVLdiUPy)** began to yield after reaching the melting temperature of the UPy dimers.

Conclusions

The results presented here show that the strong and directional hydrogen bonds in UPy telechelic polyesters can be used to prepare supramolecular copolymers in two fundamentally different ways. Functionalizing a random copolymer leads to supramolecular random copolymers, while mixing miscible telechelic homopolymers yields supramolecular segmented copolymers. In the functionalization of VL-containing diols, attention should be paid to the amount of catalyst used as it may cause depolymerization of VL segments, changing the original CL/VL ratio in the final product. The mechanical and thermal properties of the random copolymers and the segmented copolymers are different. In the random copolymer, the melting point of the polyester backbone is dependent on composition, and is below room temperature when the monomer ratio is close to 1, negatively affecting the mechanical properties of the material. In the supramolecular segmented copolymer, the melting point of the crystalline polyester parts is nearly independent of composition, and the modulus of the materials can be tuned by varying the composition. Both types of materials show an additional melting point ascribed to crystallinity of the UPy groups. The materials can therefore be described as supramolecular thermoplastic elastomers[51] in which the UPy moiety is microphase separated from the polyester matrix and provides mechanical strength above the melting point of the polyester.

We conclude that, of the two methods to obtain supramolecular copolymers, the mixing of two supramolecular homopolymers leads to a better control over thermal and mechanical properties. Furthermore, an advantage of blending homopolymers over the use of functionalized copolymers is that only two polymers have to be synthesized, which can be mixed in different ratios to obtain a material with the desired modulus. Using this method, it is possible to create a “library” of materials from which materials with controllable mechanical and thermal properties are obtained with minimal synthetic effort.

Acknowledgment. We thank Jolanda Spiering for her contribution to the synthesis of **p(CL-*co* 33% VL)diUPy**, Freek Hermans for help with the synthesis, and Prof. E. W. Meijer for useful discussions. Financial support (DJMvB) from NanoNed, the nanotechnology program of the Dutch Ministry of Economic Affairs (Grant EPC. 6338) is gratefully acknowledged.

Supporting Information Available: Text giving experimental procedures and data for ^{1}H NMR and ^{13}C NMR spectra of the high molecular weight polymers, polymer diols, and supramolecular polymers, including calculation of the molecular weights and schemes showing their structures, and depolymerization and GPC data on **pVL-diol**, **pCL-diol**, and **p(CL-*co* 50% VL)diUPy** in the presence and absence of DBTDL, including figures showing GPC plot. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Freier, T. *Adv. Polym. Sci.* **2006**, *203*, 1−61.
(2) Engelberg, I.; Kohn, J. *Biomaterials* **1991**, *12*, 292−304.
(3) Scholes, P. D.; Coombes, A. G. A.; Illum, L.; Davis, S. S.; Vert, M.; Davies, M. C. *J. Controlled Release* **1993**, *25*, 145−153.
(4) Stridsberg, K. M.; Ryner, M.; Albertsson, A.-C. *Controlled-Ring-Opening Polymerization: Polymers with designed Macromolecular Architecture*; Springer: Berlin and Heidelberg, Germany, 2002; Vol. 157/2001; pp 41−65.
(5) Gruvegård, M.; Lindberg, T.; Albertsson, A.-C. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 885−902.
(6) Agrawal, C. M.; Ray, R. B. *J. Biomed. Mater. Res.* **2001**, *55*, 141−150.
(7) Parrish, B.; Quansah, J. K.; Emrick, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1983−1990.
(8) Cha, Y.; Pitt, C. G. *Biomaterials* **1990**, *11*, 108−112.
(9) Qui, Z.; Fujinami, S.; Komura, M.; Nakajima, K.; Ikehara, T.; Nishi, T. *Macromol. Symp.* **2004**, *216*, 255−263.
(10) Tsuji, H.; Ikada, Y. *J. Appl. Polym. Sci.* **1998**, *67*, 405−415.
(11) Kuo, S. W.; Huang, C. F.; Chang, F. C. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1348−1359.
(12) Jutier, J. J.; Lemieux, E.; Prud’homme, R. E. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 1313−1329.
(13) Coleman, M. M.; Moskala, E. J. *Polymer* **1983**, *24*, 251−257.
(14) An, J. H.; Kim, H. S.; Chung, D. J.; Lee, D. S. *J. Mater. Sci.* **2001**, *36*, 715−722.
(15) Ceccorulli, G.; Scandola, M.; Kumar, A.; Kalra, B.; Gross, R. A. *Biomacromolecules* **2005**, *6*, 902−907.
(16) Soppimath, K. S.; Aminabhavi, T. M.; Kulkarni, A. R.; Rudzinski, W. E. *J. Controlled Release* **2001**, *70*, 1−20.
(17) Raquez, J. M.; Degée, P.; Narayan, R.; Dubois, P. *Polym. Degrad. Stab.* **2004**, *86*, 159−169.
(18) Faÿ, F.; Linossier, I.; Langlois, V.; Renard, E.; Vallée-Réhel, K. *Biomacromolecules* **2006**, *7*, 851−857.
(19) Storey, R. F.; Herring, K. R.; Hoffman, D. C. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1759−1777.
(20) Rapoport, N.; Pitt, W. G.; Sun, H.; Nelson, J. L. *J. Controlled Release* **2003**, *91*, 85−95.
(21) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761−6769.
(22) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874−878.
(23) Dankers, P. Y. W.; Harmsen, M. C.; Brouwer, L. A.; van Luyn, M. J. A.; Meijer, E. W. *Nat. Mater.* **2005**, *4*, 568−574.
(24) Dankers, P. Y. W.; van Leeuwen, E. N. M.; van Gemert, G. M. L.; Spiering, A. J. H.; Harmsen, M. C.; Brouwer, L. A.; Janssen, H. M.; Bosman, A. W.; van Luyn, M. J. A.; Meijer, E. W. *Biomaterials* **2006**, *27*, 5490−5501.
(25) Kautz, H.; van Beek, D. J. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **2006**, *39*, 4265−4267.
(26) Keizer, H. M.; van Kessel, R.; Sijbesma, R. P.; Meijer, E. W. *Polymer* **2003**, *44*, 5505−5511.
(27) Binder, W. H.; Kunz, M. J.; Ingolic, E. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 162−172.
(28) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 13986−13987.
(29) Kluger, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 485−499.
(30) Park, T.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 14236−14237.
(31) Binder, W. H.; Bernstorff, S.; Kluger, C.; Petraru, L.; Kunz, M. J. *Adv. Mater.* **2005**, *17*, 2824−2828.
(32) Yang, X.; Hua, F.; Yamato, K.; Ruckenstein, E.; Gong, B.; Kim, W.; Ryu, C. Y. *Angew. Chem., Int. Ed.* **2004**, *116*, 6633−6636.
(33) Scherman, O. A.; Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 11850−11855.
(34) Lecomte, P.; Stassin, F.; Jérôme, R. *Macromol. Symp.* **2004**, *215*, 325−338.
(35) Biela, T.; Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromol. Symp.* **2006**, *240*, 47−55.
(36) Trinkle, S.; Hoffmann, B.; Kricheldorf, H. R.; Friedrich, C. *Macromol. Chem. Phys.* **2001**, *202*, 814−823.
(37) de Geus, M.; Peeters, J.; Wolffs, M.; Hermans, T.; Palmans, A. R. A.; Koning, C. E.; Heise, A. *Macromolecules* **2005**, *202*, 814−823.
(38) Srivastava, R. K.; Albertsson, A. C. *Macromolecules* **2006**, *39*, 46−54.
(39) Kobayashi, S.; Uyama, H.; Kimura, S. *Chem. Rev.* **2001**, *101*, 3793−3818.
(40) van der Mee, L.; Helmich, F.; de Bruijn, R.; Vekemans, J. A. J. M.; Palmans, A. R. A.; Meijer, E. W. *Macromolecules* **2006**, *39*, 5021−5027.
(41) Bankova, M.; Kumar, A.; Impallomeni, G.; Ballistreri, A.; Gross, R. A. *Macromolecules* **2002**, *35*, 6858−6866.
(42) Kobayashi, S.; Uyama, H.; Namekawa, S.; Hayakawa, H. *Macromolecules* **1998**, *31*, 5655−5659.
(43) van der Mee, L.; Antens, J.; van der Kruijs, B.; Palmans, A. R. A.; Meijer, E. W. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2166−2176.

(44) Peeters, J.; Palmans, A. R. A.; Veld, M.; Scheijen, F.; Heise, A.; Meijer, E. W. *Biomacromolecules* **2004**, *5*, 1862−1868.

(45) Saotome, K.; Kodaira, Y. *Makromol. Chem.* **1965**, *82*, 41−52.

(46) Elzein, T.; Nasser-Eddine, M.; Delaite, C.; Bistac, S.; Dumas, P. *J. Colloid Interface Sci.* **2004**, *273*, 381−387.

(47) Coleman, M. M.; Zarian, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 837−850.

(48) Furuhashi, Y.; Sikorski, P.; Atkins, E.; Iwata, T.; Doi, Y. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 2622−2634.

(49) Söntjens, S. H. M. Ph.D. Thesis. Technische Universiteit Eindhoven, Eindhoven, The Netherlands, 2002.

(50) Beijer, F. H. Ph.D. Thesis. Technische Universiteit Eindhoven, Eindhoven, The Netherlands, 1998.

(51) Legge, N. R.; Holden, G. *Thermoplastic Elastomers: A Comprehensive Review*; Carl Hansser Verslag: New York, 1978.

MA0705927