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Combining Covalent and Noncovalent Cross-Linking: A Novel Terpolymer for Two-Step Curing Applications

Abdelkrim El-ghayoury,[†,‡] Harald Hofmeier,[†] Barteld de Ruiter,[‡] and Ulrich S. Schubert*[,†]

Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and Functional Polymers and Coatings, TNO Industrial Technology, De Rondom 1, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands

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ABSTRACT: A terpolymer of poly(butyl acrylate) bearing terpyridine as well as oxetane units was synthesized by free radical polymerization and characterized using NMR, UV−vis, and GPC. Subsequently, UV−vis experiments indicated clearly a noncovalent cross-linking of the terpyridine moieties by addition of iron(II) ions. Moreover, the ability of covalent cross-linking was studied by polymerizing the oxetane rings utilizing Lewis acids. IR spectroscopy and DSC experiments clearly revealed the success of the combination of both steps when utilizing iron(II) ions and $AlCl_3$.

Introduction

Copolymers containing supramolecular entities[1] as well as covalent cross-linking units[2] raised special interest during the past years due to their possibilities to construct novel materials with smart or addressable properties, such as switchable adhesives or self-repairing and self-healing materials or coatings.[3] For this purpose, the reversible and weaker features of noncovalent interactions have to be combined with the known covalent chemistry.[4] Free radical polymerization is a versatile method for rapid and efficient (co)polymerization of a variety of (un)functionalized (meth)acrylate monomers.[5] Easily handable polymers, block copolymers, or graft copolymers, bearing different functional groups, can therefore be obtained. On the other hand, oxetane is a nicely polymerizable unit that yields functional polyethers through a ring-opening process[6−8] and possesses a higher photoinitiated polymerization ability than oxiranes.[9] This behavior makes them in particular attractive for UV-curable processes in coatings technology.[10] In the past years supramolecular chemistry developed into a well-accepted field where defined supramolecular architectures are generated through self-assembly processes.[11] Within this field, supramolecular polymers in which noncovalent interactions are combined with covalent chemistry appear to be of great interest as new functional polymeric systems.[12,13] As supramolecular systems, mainly hydrogen-bonding[14] and metal−ligand[15,16] units are utilized at present. For the latter one, 2,2′:6′,2″-terpyridine ligands are one of the most prominent building blocks due to their well-known chelating effect for a wide range of transition-metal ions.[17,18]

An interesting approach would be the design of copolymers and terpolymers that contain both a supramolecular (noncovalent and reversible) cross-linking moieties as well as a unit, which can be covalently cross-linked. Here we report on the synthesis and characterization of an acrylate terpolymer bearing a terpyridine moiety as a supramolecular unit and an oxetane moiety as a covalent cross-linking unit as well as on the first covalent and noncovalent cross-linking studies (Figure 1).

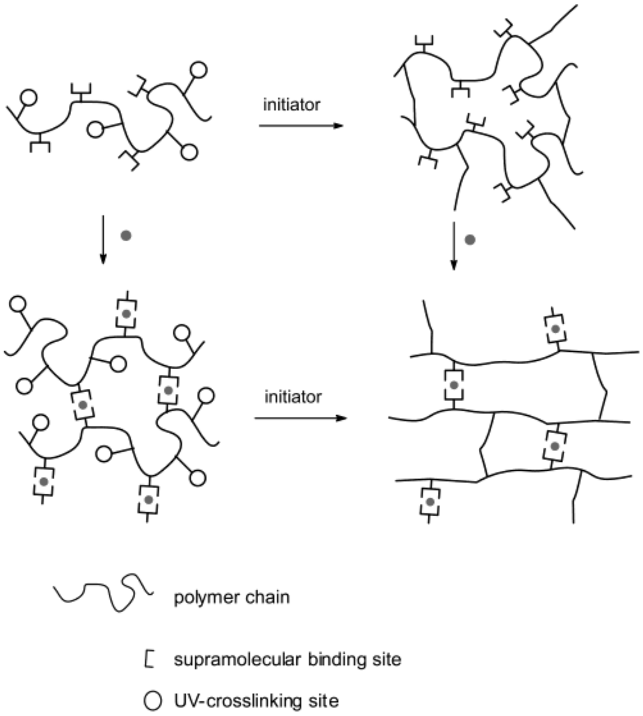

Figure 1. Overview of the two-step covalent and supramolecular cross-linking.

Experimental Part

Materials and Instrumentation. Basic chemicals were obtained from Sigma-Aldrich. 4′-Hydroxypropyl-2,2′:6′,2″-terpyridine (**1**) was prepared from 4′-chloroterpyridine[19] as described in refs 16b and 20. The acrylate−oxetane monomer **5** was prepared in a four-step synthesis as described elsewhere:[2c] 2-Bromoethanol was protected according to a literature procedure, yielding the protected bromoethanol.[21] The protected alcohol was reacted with 3-ethyl-3-hydroxymethyl-

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[†] Eindhoven University of Technology and Dutch Polymer Institute.

[‡] Functional Polymers and Coatings, TNO Industrial Technology.

* Corresponding author: Fax +31-(0)40-2474186; e-mail u.s.schubert@tue.nl.

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oxetane under phase transfer catalyst conditions to afford the substituted oxetane. The deprotection of the latter compound using the pyridinium−*p*-toluenesulfonic salt yielded the hydroxyethyloxetane (**4**). This compound was finally reacted with acryloyl chloride (**2**) and triethylamine in dichloromethane to afford the desired acrylate−oxetane (**5**). The butyl acrylate monomer was freshly distilled before use. Preparative size exclusion chromatography was carried out on BioBeads SX1 columns (CH_2Cl_2). NMR spectra were measured on a Varian Mercury 400 and a Varian Gemini 300 NMR spectrometer. The chemical shifts were calibrated to the residual solvent peaks or TMS. UV−vis spectra were recorded on a Perkin-Elmer Lamda-45 (1 cm cuvettes), and IR spectra were taken on a Perkin-Elmer Spectrum-1 ATR-FT-IR spectrometer. DSC investigations were performed on a Perkin-Elmer Pyris-1 DSC system with a heating rate of 40 K/min (T_g). GPC measurements were performed on a Shimadzu GPC apparatus using a 5 μm PL-gel-mixed-D column (cross-linked polystyrene) with chloroform as eluent and a UV as well as an RI detector.

Acrylic Acid 3-(2,2′:6′,2″-Terpyridin-4′-yloxy)propyl Ester (3). To a solution of 4′-(hydroxypropyloxy)-2,2′:6′,2″-terpyridine (**1**) (1.0 g, 3.25 mmol) in 50 mL of ice-cooled CH_2Cl_2 were added 320 mg (3.57 mmol, 0.288 mL) of acryloyl chloride (**2**) and 493.3 mg (4.88 mmol, 0.5 mL) of triethylamine via a syringe. After 30 min, the solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was extracted with an aqueous solution of K_2CO_3 (3 × 15 mL) to neutralize and remove the inorganic salts. The solvent was removed in vacuo at room temperature, and the product was recrystallized twice from methanol (10 mL) to yield 800 mg (66%) of **3** as white crystals; mp 90 °C. ^1H NMR (400 MHz, CH_3CN): δ (ppm) = 2.23 (tt, 2 H, J = 6.04 Hz, CH_2), 4.34 (t, 4 H, J = 6.04 Hz, OCH_2), 4.39 (t, 4 H, J = 6.04 Hz, OCH_2), 5.82 (dd, 1 H, J = 10.44, 1.10 Hz, H(olefinic)), 6.13 (dd, 1 H, J = 17.58, 10.44 Hz, H(olefinic)), 6.42 (dd, 1 H, J = 17.58, 1.10 Hz, H(olefinic)) 7.40 (m, 2 H, $H_{5,5''}$), 7.91 (ddd, 2 H, J = 8.06, 8.06, 2.20 Hz, $H_{4,4''}$), 7.98 (s, 2 H, $H_{3',5'}$), 8.61 (d, 2 H, J = 8.06 Hz, $H_{3,3''}$), 8.67 (d, 2 H, J = 5.86 Hz, $H_{6,6''}$). GC-MS: m/z = 361.2 (M^+). UV−vis (CH_3CN): λ_{max} (ϵ) = 276 (24 200), 240.4 (26 320) nm (L mol^{-1} cm^{-1}).

Poly(butyl acrylate)-*co*-(2-methylacrylic acid 3-(2,2′:6′,2″-terpyridin-4′-yloxy)propyl ester)-*co*-acryloxetane (7). 437 mg (3.41 mmol) of butyl acrylate (**6**), 250 mg (1.25 mmol) of **3**, and 106 mg (0.29 mmol) of **5** were dissolved in 2 mL of *p*-xylene and heated to 87 °C. Subsequently, 12 mg (0.07 mmol) of azobis(isobutyronitrile) (AIBN) was added, and heating was continued for 10 h. The mixture was precipitated twice in 20 mL of pentane followed by preparative size exclusion chromatography, yielding 556 mg (70%) of **7** as a white sticky solid. ^1H NMR (400 MHz, $CHCl_3$): δ = (ppm) 0.97 (b, 57 H, CH_3), 1.39 (b, 43 H, CH_2), 1.62 and 1.89 (b, 30 H, CH_2), 2.19 (m (b), 2 H, CH_2), 4.03 (s, 28 H, OCH_2), 4.19 (m (b), 10 H, OCH_2), 4.36 (d, 10 H, J = 5.13 Hz, oxetane), 4.43 (d, 10 H, J = 5.68 Hz, oxetane), 7.32 (m, 2 H, $H_{5,5''}$), 7.83 (dd, 2 H, J = 8.06, 8.06 Hz, $H_{4,4''}$), 8.02 (s, 2 H, $H_{3',5'}$), 8.61 (d, 2 H, J = 8.06 Hz, $H_{3,3''}$), 8.67 (d, 2 H, J = 5.86 Hz, $H_{6,6''}$). UV−vis ($CHCl_3$): λ_{max} (ϵ) = 279 (52 300), 246 (54 800) nm (L mol^{-1} cm^{-1}). GPC ($CHCl_3$): $\bar{M}_n = 7400$, PDI = 2.46. $T_g = -23.5$ °C.

UV Titration of 7. 4.1 mg of **7** was dissolved in 50 mL of argon-saturated chloroform. A 1.62×10^{-4} M solution of iron(II) chloride (in argon-saturated methanol) was added in steps of 40 μL while the mixture was stirred. 30 min after every addition a UV−vis spectrum was recorded. The absorption value of the maximum of the metal to ligand charge-transfer band (MLCT) at 558 nm was used in order to obtain the titration curve.

Cross-Linking of the Terpolymer 7. *Route a:* 24 mg of terpolymer **7** was dissolved in 2 mL of nitromethane and saturated with argon. Subsequently, 5 drops of borontetrafluorate etherate were added, and the mixture was heated to 60 °C overnight. The resulting material was dried in a vacuum. Yield: 18 mg.

Route b: 16 mg of **7** was dissolved in 1 mL of dichloromethane. Then 1 mL of a solution of $AlCl_3$ in dichloromethane was added, and the mixture was allowed to react overnight.

Route c: To 18 mg of **7** in dichloromethane was added 1 mg of iron(II) chloride in 0.2 mL of methanol. Half of this solution was treated as described in (b).

Route d: The material obtained from (a) was covered with dichloromethane, and 3 drops of a methanolic solution of $FeCl_2$ were added.

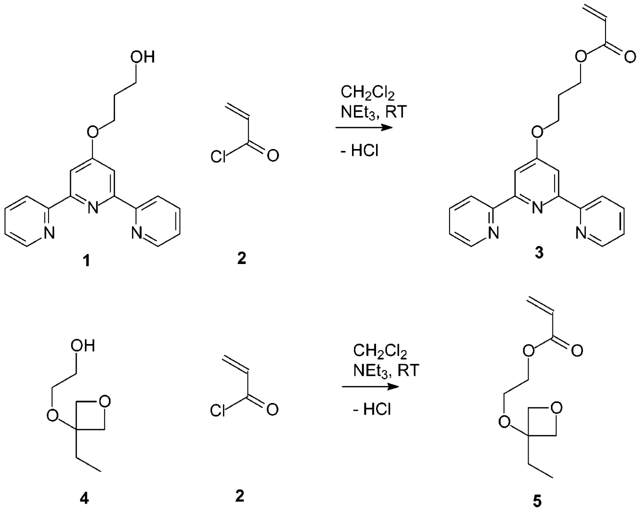
Results and Discussion

In this contribution we focus on a first proof of principle study that combines a metallo-supramolecular moiety (terpyridine metal complexes) with a covalent ring-opening entity (oxetane functions) in a terpolymer structure (Figure 1). Addition of suitable metal ions (such as iron(II), zinc(II), copper(II), or cobalt(II) salts) should immediately lead to the formation of the corresponding metal complexes and therefore to a noncovalent cross-linking (see e.g. refs 16a and 24a for the cross-linking of terpyridine-containing copolymers). In this case, partially cross-linked materials with adjustable viscosity behavior (directly tunable by the number of the noncovalent cross-linking units and the kind of metal ions (cross-linkers)) can be obtained. This has already been demonstrated on PMMA copolymers containing terpyridines where the solution viscosity could be increased by the factor up to 20 through addition of copper(II),[24a] zinc(II), or iron(II) ions.[24b] In addition, also the ruthenium(II/III) chemistry could be utilized in order to further control the cross-linking step (see refs 16b and 22). It could be demonstrated recently that the supramolecular connection can be opened again utilizing redox processes as well as pH or temperature changes.[23] Moreover, the ring-opening polymerization of the oxetane moiety (utilizing a Lewis acid or a photoinitiator) would create a “classical” covalently cross-linked system. Applying that process after the supramolecular cross-linking step would finally fix the supramolecular cross-linked structure by the formation of polyether bonds. In addition, the process could also be reversed, resulting first in a covalently cross-linked material with the ability to further undergo supramolecular cross-linking and therefore opening the possibility to react on potential changes or damages.

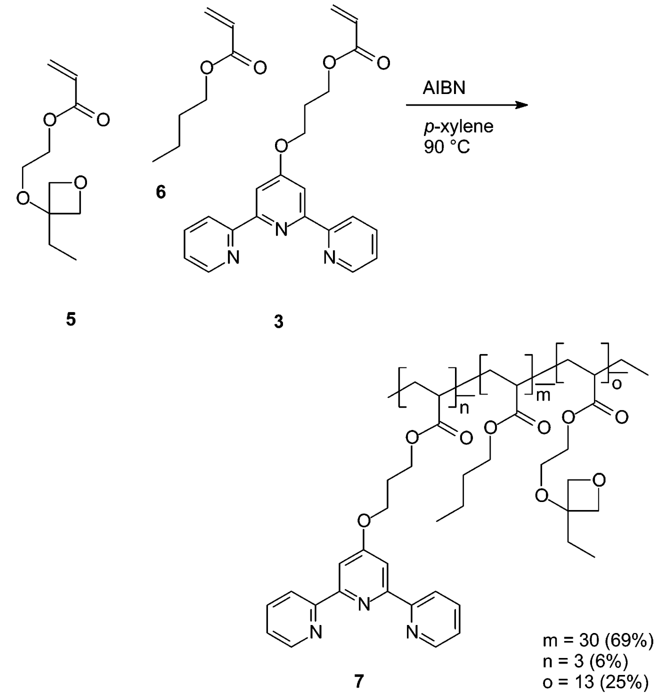
To create a suitable polymer system with both terpyridine and oxetane moieties in the main chain, a free radical polymerization process was chosen in combination with acrylate units as polymerizable groups. The terpyridine monomer was synthesized starting from the commercial 4′-chloroterpyridine[19] compound. A C_3-spacer was introduced by a nucleophilic substitution reaction in order to avoid any interference of the rather bulky terpyridine unit with the polymerizable group during the terpolymerization process (Scheme 1).[16b,20] The acrylate was prepared by reaction of acryloyl chloride with the hydroxyl-terminated terpyridine **1** in 66% yield. The oxetane monomer **5** was obtained in a four-step reaction introducing a C_2-spacer in between the acrylate and the oxetane ring in order to avoid intramolecular ring-formation during the ring-opening process (see ref 2c and Experimental Part). Moreover, butyl acrylate **6** was chosen as third monomer due to its low T_g, which was expected to be of benefit during the cross-linking experiments.

Subsequently, monomers **3** (6%), **5** (25%), and **6** (69%) were polymerized with *N*,*N*-azobis(isobutyronitrile) (AIBN) in order to result the desired butyl acrylate terpolymer **7** bearing both terpyridine and oxetane units (Scheme 2). The polymer was isolated and purified by precipitation and preparative size exclusion chroma-

Scheme 1. Synthesis of the Comonomers 3 and 5



Scheme 2. Synthesis of Terpolymer 7



tography in 70% yield as a white sticky solid. A comparison of the ^{1}H NMR spectra of the corresponding monomers **3** and **5** with the isolated polymer **7** revealed that all functional groups were incorporated into the terpolymer (Figure 2). The terpyridine protons could be observed between 7 and 9 ppm, and the cyclic OCH$_2$-oxetane signals appeared at 4.36 and 4.43 ppm in combination with the other OCH$_2$ signals. In the region from 0.5 to 2.5 ppm the aliphatic protons were detected. The absence of any olefinic signals in the spectrum of polymer **7** underlined the successful isolation and purification procedure. From the integral ratios (combined with the results of the UV−vis titration; see below), a terpyridine content of 5% and an oxetane content of 28% could be calculated. These values are in good agreement with the original composition of the monomer mixture: Obviously, the three monomers were built into the final terpolymer according to the original monomer feed. The GPC analysis (chloroform, polystyrene standards) revealed an $\bar{M}_n$ of 7400 g/mol and polydispersity index of 2.46. It has to be mentioned that the terpyridine units usually interact with the column material resulting in apparent lower molar mass values.

To gain information regarding the amount of terpyridine units incorporated into each terpolymer chain and to investigate the noncovalent cross-linking behavior, a UV−vis titration with iron(II) ions was performed: A UV−vis spectrum was recorded after each addition of an aliquot of metal salt (in methanol) to polymer **7** (in chloroform; see Figure 3). The appearance of the characteristic metal to ligand charge-transfer absorption band (MLCT) is a clear proof for the complexation of the terpyridine units with iron(II) ions. By monitoring the intensity of the MLCT band at 558 nm, a titration curve was obtained (Figure 3, inset). By this method, a terpyridine content of 2.8 terpyridines per polymer chain was calculated. No change of the absorption bands has been observed with time.[24] In addition, the titration results also revealed a successful cross-linking of the terpolymer: When the experiment was conducted in a higher concentration, a precipitation of the colored metal-containing terpolymer could be observed.

The covalent cross-linking possibilities were investigated utilizing different Lewis acids in order to open the oxetane rings. First, terpolymer **7** was treated with boron trifluorate etherate and heated to 60 °C overnight. A rubberlike, insoluble material was obtained after the reaction. The transmission FTIR spectra depicted in Figure 4 showed a significant decrease of the oxetane C−O−C band at 980 cm^{-1}, indicating that the cationic ring-opening polymerization took place. Moreover, DSC measurements revealed no glass transition anymore, indicating that the linear terpolymer **7** was cross-linked via the opening of the oxetane side groups (Figure 5). The DSC curve of the corresponding terpolymer **7** before that treatment is also displayed in Figure 5. In this case a glass transition temperature (T_g) of −23.5 °C could be observed, caused by the large amount of butyl acrylate in the polymer.

Subsequently, a first experiment regarding the coupling of supramolecular and covalent cross-linking was performed. The addition of a corresponding amount of iron(II) ions (calculated from the UV−vis titration results) to a diluted solution of terpolymer **7** resulted in a deep purple solution (experimental part, route a). This loosely noncovalently cross-linked polymer was then treated in a second step with boron trifluorate etherate to initiate the cationic ring-opening of the oxetane side chains (Experimental Part, route a). However, this procedure resulted in a complete disappearance of the purple color, indicating a decomplexation of the terpyridine units. These findings can be explained by a reaction of boron trifluorate etherate (strong Lewis acid) and the terpyridine moiety (base), resulting in a decomplexation of the terpyridine metal complexes. To circumvent this problem, the initiator was changed as well as the reaction conditions. In the next experiments, the reaction was performed at room temperature in dichloromethane utilizing aluminum trichloride as initiator for the ring-opening polymerization of the oxetane side chains (Experimental Part, route b). The effect of this treatment to the terpolymer **7** is shown in Figure 4. Also in this case, a significant decrease of the oxetane C−O−C band at 980 cm^{-1} could be observed, indicating a successful ring-opening process. After this positive result, AlCl$_3$ was utilized for the two-step cross-linking experiment. A sample of supramolecular cross-linked

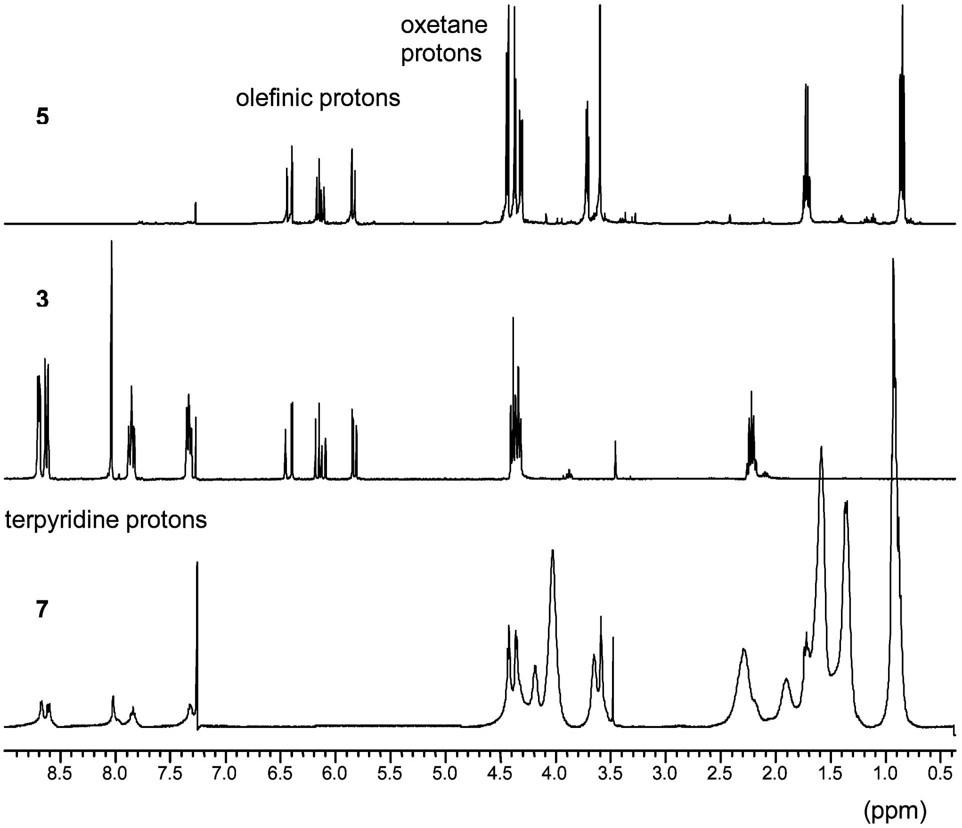


Figure 2. NMR spectra of the comonomers **3**, **5**, and the resulting terpolymer **7** (in $CDCl_3$).

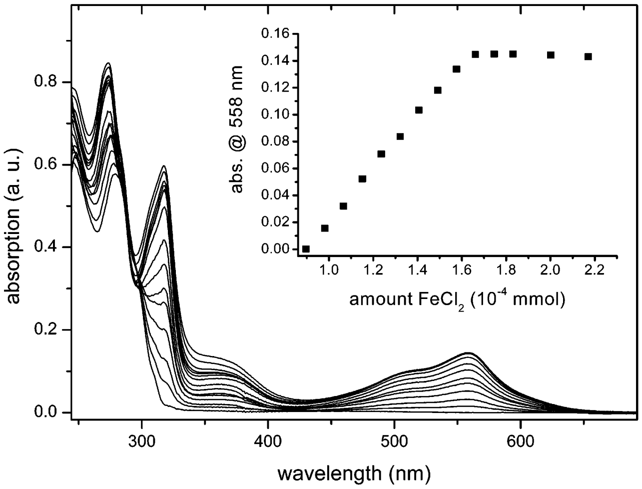


Figure 3. UV titration of **7** with $FeCl_2$ (in chloroform).

terpolymer **7** was treated under the above-described conditions with $AlCl_3$ (Experimental Part, route c). This time, the characteristic deep purple color did not fade away. The FTIR spectra shown in Figure 6 revealed a significant decrease of the oxetane C–O–C peak at 980 cm^{-1}. These results indicate that both the supramolecular and covalent cross-linking steps could be combined. In a second approach, the order of the cross-linking reactions was reverted: The rubberlike material obtained from cross-linking of the uncomplexed terpolymer with $AlCl_3$ (Experimental Part, route b) was exposed to a methanolic solution of iron(II) chloride (Experimental Part, route d). The color immediately turned to purple, which indicated that a complexation of the accessible terpyridine groups took place.

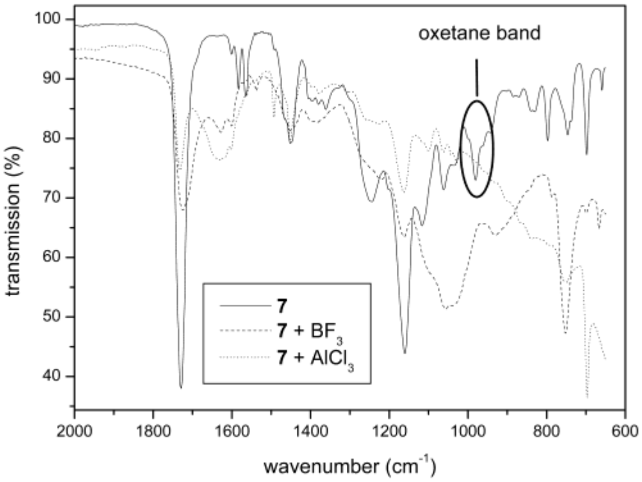


Figure 4. IR spectra of **7** before and after cross-linking with $BF_3 \cdot Et_2O$ and $AlCl_3$.

Conclusion

We have synthesized and characterized a terpolymer via free radical polymerization containing both a terpyridine and an oxetane moiety. The first one is able to complex metal ions, and the latter one can be used for cationic ring-opening polymerizations, e.g., activated by Lewis acids as well as by photoinitiators. The terpyridine unit was chosen due to its outstanding ability to form stable but also reversible complexes with a wide variety of transition metal ions. The terpolymer was characterized by NMR, DSC, UV–vis titration, and GPC, revealing an $\bar{M}_n$ of 7400 g/mol and an average terpyridine content of 2.8 per polymer chain. Noncovalent and covalent cross-linking experiments were performed using iron(II) ions, boron trifluorate etherate and

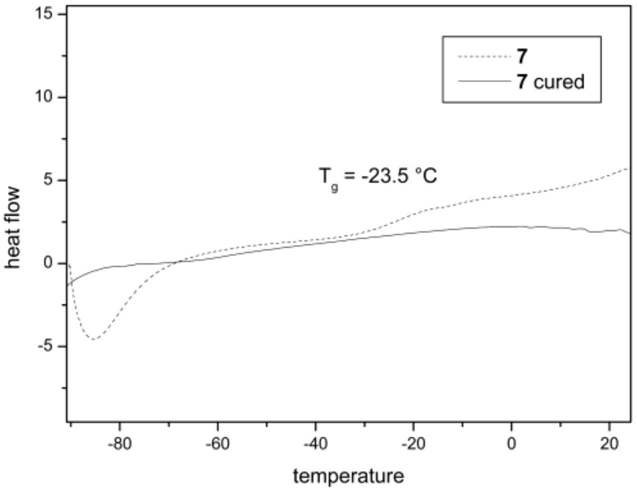


Figure 5. DSC curves of **7** before and after cross-linking with $BF_3{\cdot}Et_2O$.

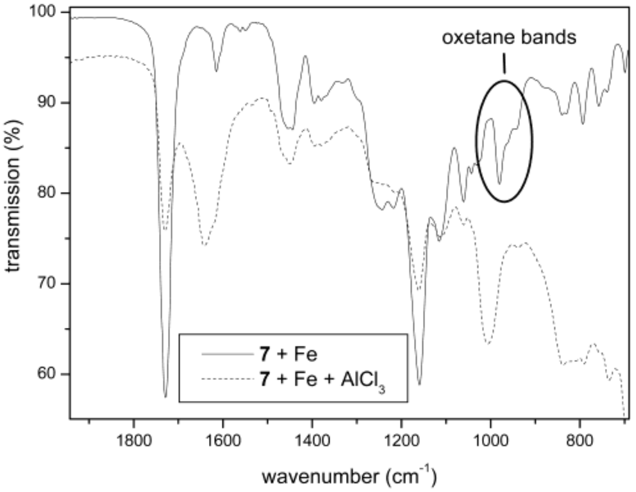


Figure 6. IR spectra of the iron(II) complex of **7** before and after cross-linking with $AlCl_3$.

aluminum trichloride. The latter one could successfully be combined with the iron(II) complexation. These results create multiple possibilities for two-step cross-linking procedures and open new avenues for the development of novel materials, e.g., smart coatings with self-healing properties. More detailed studies concerning cross-linking details (cross-linking efficiency), use of terpolymers with higher molar masses and different comonomer compositions, use of other covalent cross-linking groups such as oxiranes, and the introduction of photoinitiated ring-opening processes are currently in progress.

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References and Notes

(1) (a) Rieth, L. R.; Eaton, R. F.; Coates, G. W. *Angew. Chem.* **2001**, *113*, 2211; *Angew. Chem., Int. Ed.* **2001**, *40*, 2153. (b) Chino, K.; Ashiura, M. *Macromolecules* **2001**, *34*, 9201.

(2) (a) Roffey, C. C. *Photopolymerization of Surface Coatings*; Wiley: Chichester, England, 1982. (b) Pappas, S. P. *UV-Curing Science and Technology*; Technology Marketing: Stanford, CT, 1978 and 1985; Vols. 1 and 2. (c) El-Ghayoury, A.; Boukaftane, C.; De Ruiter, B.; van der Linde, R. *J. Polym. Sci., Part A* **2003**, *414*, 469.

(3) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W. *MRS Bull.* **2000**, *25*, 49.

(4) (a) Lehn, J.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *69*, 1. (b) Abstracts of the Smart Coatings Conference, Berlin, 2002. (c) Hofmeier, H.; Schubert, U. S. *Polym. Prepr.* **2003**, *44*, 91.

(5) Moad, G. Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science: Oxford, England, 1995.

(6) Reviews on the cationic ring-opening polymerization of oxetane: (a) Dreyfuss, M. P. Oxetane Polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley and Sons: New York, 1987; p X/751. (b) Penzek, S.; Kubisa, P. Cationic Ring-Opening Polymerization: Ethers. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: Oxford, 1989; p III/751. (c) Desai, H. Telechelic Polyoxetanes. In *Polymeric Materials Encyclopedia;* Salamone, J. C., Ed.; CRC Press: New York, 1996; p XI/8286.

(7) Xu, Y.; Ogawa, H.; Kanoh, S.; Motoi, M. *Polym. J.* **1999**, *31*, 143.

(8) Decker, C. *Macromol. Symp.* **1999**, *143*, 45.

(9) Sasaki, H. Design and Application of Photo-Curable Oxetane System. Ph.D. Thesis, Hokkaido, Japan, 1996.

(10) Sasaki, H.; Crivello, J. V. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 915.

(11) (a) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Schubert, U. S. In *Tailored Polymers & Applications;* Mishra, M., Yagci, Y., Nuyken, O., Ito, K., Wnek, G., Eds.; VSP Publishers: Utrecht, 2000; p 63.

(12) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.

(13) Schubert, U. S.; Eschbaumer, C. *Angew. Chem.* **2002**, *114*, 3016; *Angew. Chem., Int. Ed.* **2002**, *41*, 2892.

(14) (a) Stadler, R.; de Araujo, M. A., Kuhrau, M., Rösch, J. *Makromol. Chem.* **1989**, *190*, 1433. (b) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J.; Hirschberg, J. H.; Lange, R. F.; Lowe, J. K.; Meijer, E. W. *Science* **1997**, *278*, 1601.

(15) (a) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1993**, *26*, 6315. (b) Eisenbach, C. D.; Schubert, U. S. *Macromolecules* **1993**, *26*, 7372. (c) Chujo, Y.; Naka, A.; Krämer, M.; Sada, K.; Saegusa, T. *Pure Appl. Chem.* **1995**, *A32*, 1213. (d) Lamba, J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801. (e) Schütte, M.; Kurth, D. G.; Linford, M. R.; Cölfen, H.; Möhwald, H. *Angew. Chem.* **1998**, *110*, 3058; *Angew. Chem., Int. Ed.* **1998**, *37*, 2891. (f) Kelch, S.; Rehahn, M. *Macromolecules* **1999**, *32*, 5818. (g) Kelch, S.; Rehahn, M. *Chem. Commun.* **1999**, 1123. (h) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 1341. (i) McAlvin, J. E.; Scott, S. B.; Fraser, C. L. *Macromolecules* **2000**, *33*, 6953. (j) Hien, O.; Eschbaumer, C.; Schubert, U. S. *Macromol. Rapid Commun.* **2000**, *21*, 1156. (k) Schubert, U. S.; Heller, M. *Chem.—Eur. J.* **2001**, *7*, 5252. (l) Corbin, P. S.; Webb, M. P.; McAlvin, J. E.; Fraser, C. L. *Biomacromolecules* **2001**, *2*, 223.

(16) (a) Hanabusa, K.; Nakano, K.; Koyana, T.; Shirai, H.; Hojo, N.; Kurose, A. *Makromol. Chem.* **1990**, *191*, 391. (b) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, *23*, 561.

(17) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(18) Schubert, U. S.; Eschbaumer, C.; Andres, P. R.; Hofmeier, H.; Weidl, C. H.; Herdtweck, E.; Dulkeith, E.; Morteani, A.; Hecker, N. E.; Feldmann, J. *Synth. Met.* **2001**, *121*, 1249.

(19) Schubert, U. S.; Schmatloch, S.; Precup, A. A. *Design. Monom. Polym.* **2002**, *5*, 211.

(20) Sampath, U.; Putnam, W. C.; Osiek, T. A.; Touami, S.; Xie, J.; Cohen, D.; Cagnolini, A.; Droege, P.; Klug, D.; Barnes, C. L.; Modak, A.; Bashkin, J. K.; Jurisson, S. S. *J. Chem. Soc., Dalton Trans.* **1999**, 2049.

(21) Arisawa, M.; Kato, C.; Kaneko, H.; Nishida, A.; Nakagawa, M. *J. Chem. Soc., Perkin Trans 1* **2000**, 1873.

(22) (a) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromolecules* **2002**, *35*, 4560. (b) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem.* **2002**, *114*, 3980; *Angew. Chem., Int. Ed.* **2002**, *41*, 3825.

(23) (a) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1993**, *26*, 6320. (b) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, *22*, 1358. (c) Schmatloch, S.; González, M. F.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 957.

(24) (a) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090. (b) Hofmeier, H.; Schubert, U. S. *Macromol. Chem. Phys.*, in press.

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