brane lipid structure of thermophilic bacteria. The synthetic steps involved in preparing the molecule are few. This system forms stable sheets, ribbons, and vesicles with little or no tendency to twist into helical structures or tubules as is the case in systems based on the typical mesophilic lipid structure.[27] This propensity to form sheets and ribbons should facilitate the fabrication of planar device elements. In addition to an extremely large bandwidth for fluorescence excitation and emission, the material displays mechanochromic phenomena. The strips were easily metallized, allowing the potential fabrication of systems with a metallic conducting element separated from an organic conducting element by an insulating layer of alkane chains. Liposomes made from this system are regular and are also readily polymerizable as evidenced by their rapid and dramatic color change on irradiation with UV light. The availability of these new materials significantly increases the potential applications and the range of stable polydiacetylene superstructures that are accessible.

Experimental

Laser scanning confocal microscopy was performed on a Zeiss 210 instrument with a 488 nm laser. Images were obtained in the bright field, darkfield, phase contrast, and polarization modes. For the polarizing mode experiments, an analyzing cross-polarizer was placed on the objective lens and rotated until light cancellation. Conventional light microscopy was conducted in the bright field and phase contrast modes using tungsten illumination. A mercury lamp was used for illumination in the fluorescence detection mode.

To effect self-assembly into layers, the lipid (10 mg) was dissolved in 0.5 mL chloroform, 9.5 mL ethanol, or 10 mL of ethanol. Water (0.1 mL) was added to a portion of this solution (0.25 mL). Some preparations contained acetic acid or trifluoroacetic acid in amounts 0.5, 1, 5, or 10 times the number of moles of lipid. Samples were incubated at 25 °C. The samples were observed after several hours up to 2–3 days. In the metallization experiments, samples were prepared as described above except that the water contained 5–10 equiv. copper(II) or nickel(II) sulfate. A suspension of the nickel-impregnated structures in water was placed on a microscope slide, excess metal ions was removed and ~10 equiv. of sodium borohydride was added. The slides were left for 2 h to 1 day. Supramolecular structures were polymerized by irradiation with UV light (254 nm, 6 W, 350μW/cm^2 for 3 min).

Received: December 29, 1999
Final version: March 10, 2000

[1] W. H. Kim, B. Bihari, R. Moody, N. B. Kodali, J. Kumar, S. K. Tripathy, *Macromolecules* **1995**, *28*, 642.
[2] B. I. Greene, J. Orenstein, S. Schmitt-Rink, *Science* **1990**, *247*, 679.
[3] M. Sukwattanasinitt, X. Wang, L. Li, X. Jiang, J. Kumar, S. K. Tripathy, D. J. Sandman, *Chem. Mater*. **1998**, *10*, 27.
[4] C. A. Sandstedt, C. J. Eckhardt, M. J. Downey, D. J. Sandman, *Chem. Mater*. **1994**, *6*, 1346.
[5] S. Molyneux, A. K. Kar, B. S. Wherrett, T. L. Axon, D. Bloor, *Opt. Lett.* **1993**, *18*, 2093.
[6] R. R. Chance, G. N. Patel, J. D. Witt, *J. Chem. Phys.* **1979**, *71*, 206.
[7] M. F. Rubner, D. J. Sandman, C. Velazquez, *Macromolecules* **1987**, *20*, 1296.
[8] M. Wenzel, G. H. Atkinson, *J. Am. Chem. Soc.* **1989**, *111*, 6123.
[9] N. Mino, H. Tamura, K. Ogawa, *Langmuir* **1992**, *8*, 594.
[10] A. D. Nava, M. Thakur, A. E. Tonelli, *Macromolecules* **1990**, *23*, 3055.
[11] N. B. Kodali, W. Kim, J. Kumar, S. K. Tripathy, *Macromolecules* **1994**, *27*, 6612.
[12] J. E. Ehrlich, J. D. Valera, A. Darzi, A. C. Walker, *Appl. Phys. Lett.* **1991**, *59*, 2938.
[13] D. J. Westland, V. Skarda, W. Blau, L. Costa, *Electron. Lett.* **1991**, *27*, 1327.
[14] J. H. Andrews, K. D. Singer, *Appl. Opt.* **1993**, *32*, 6703.
[15] S. A. Yamanaka, D. H. Charych, D. A. Loy, D. Y. Sasaki, *Langmuir* **1997**, *13*, 5049.
[16] P. E. Schoen, P. Yager, *J. Polym. Sci.* **1985**, *23*, 2203.
[17] D. A. Johnston, L. R. Mclean, M. A. Whittam, A. D. Clark, D. Chapman, *Biochemistry* **1983**, *22*, 3194.
[18] S. Okada, S. Peng, W. Spevak, D. Charych, *Acc. Chem. Res.* **1998**, *31*, 229.
[19] D. H. Charych, J. O. Nagy, W. Spevak, M. D. Bednarski, *Science* **1993**, *261*, 585.
[20] D. H. Charych, Q. Cheng, A. Reichert, G. Kuziemko, M. Stoh, J. O. Nagy, W. Spevak, R. C. Stevens, *Chem. Biol.* **1996**, *3*, 113.
[21] Q. Cheng, R. C. Stevens, *Adv. Mater.* **1997**, *9*, 481.
[22] A. Reichert, J. O. Nagy, W. Spevak, D. Charych, *J. Am. Chem. Soc.* **1995**, *117*, 829.
[23] J. J. Pan, D. Charych, *Langmuir* **1997**, *13*, 1365.
[24] G. Wang, R. I. Hollingsworth, *Langmuir* **1999**, *15*, 3062.
[25] G. Wang, R. I. Hollingsworth, *Langmuir* **1999**, *15*, 6135.
[26] U. Seifert, J. Shillcock, P. Nelson, *Phys. Rev. Lett.* **1996**, *77*, 5237.
[27] M. S. Spector, R. R. Price, J. M. Schnur, *Adv. Mater.* **1999**, *11*, 337.

Supramolecular Polymer Materials: Chain Extension of Telechelic Polymers Using a Reactive Hydrogen-Bonding Synthon[**]

By *Brigitte J. B. Folmer*, *Rint P. Sijbesma*,[*]
Ron M. Versteegen, *Joost A. J. van der Rijt*, and
E. W. Meijer[*]

Advanced materials possessing good mechanical properties at room temperature and having a low melt viscosity at elevated temperatures are of interest for many applications, such as hot melts and thermoplastic elastomers. The properties of low-molecular-weight telechelic polymers at room temperature can be improved significantly by functionalization of the termini with associating end groups.[1–3] At higher temperatures the end groups dissociate and the viscosity decreases. Association between end groups can be based on a variety of secondary interactions, such as van der Waals, hydrophobic, ionic interactions, or hydrogen bonding. Hydrophobically end-capped polymers (HEUR) have been thoroughly studied as rheology modifiers in, for example, water-borne coatings.[1] In these materials a reversible network is formed by clustering of the end groups. The interesting physical properties of ionomers are based on the same principle.[2] Dimerization of carboxylic acid groups was used to accomplish chain extension of poly(tetramethylene oxide) (pTHF) and polydimethylsi-

---

[*] Prof. E. W. Meijer, B. J. B. Folmer, Dr. R. P. Sijbesma,
R. M. Versteegen, J. A. J. van der Rijt
Laboratory of Macromolecular and Organic Chemistry
and Dutch Polymer Institute
Eindhoven University of Technology
PO Box 513, NL-5600 MB Eindhoven (The Netherlands)
E-mail: E.W.Meijer@tue.nl

[**] The authors gratefully acknowledge Dr. M. Masse (Shell Research) for kindly providing Kraton L2203, Dr. H. W. I. Peerlings (Bayer AG) for providing OH-telechelic polyether, polycarbonate, and polyester and B. Norder (Department of Polymer Technology, Delft University of Technology) for measuring DMTA curves and experimental advice. This work has been supported by the Netherlands Foundation for Chemical Research (CW) with financial aid from the Netherlands Organization for Scientific Research (NWO).

0935-9648/00/1206-0874 $ 17.50+.50/0

loxane oligomers.[3] Furthermore, hydrogen bonding between phenyl-urazole groups enabled chain extension of telechelic polyisobutylenes and crosslinking of polybutadienes.[4] In these polymers, relatively weak association in combination with crystallization leads to physical crosslinks, which result in materials with improved properties.

Telechelic polymers functionalized with units that dimerize without forming crystalline domains will lead to concatenation of the building blocks and to selective formation of long linear chains. A high dimerization constant of the unit is a prerequisite for obtaining chains with a high degree of polymerization. Our group has described the strong dimerization of 2-ureido-4[1H]-pyrimidinones by quadruple hydrogen bonding (Fig. 1) and the formation of linear polymeric chains of difunctional compounds.[5] Recently, we have shown that this 2-ureido-4[1H]-pyrimidinone unit (UPy unit) is suitable for functionalization of low-molecular-weight telechelic siloxanes using a hydrosilylation reaction.[6] However, this synthetic strategy is not generally applicable and requires protection/deprotection steps. Furthermore, functionalization of a trifunctional hydroxy-telechelic copolymer of ethylene oxide and propylene oxide with UPy end groups has been described that used a diisocyanate possessing controlled reactivity of the two isocyanate groups.[7] But the use of this synthetic methodology is hampered by the possibility of covalent crosslinking.

Here we present the large-scale synthesis, from cheap commercially available reagents, of synthon **1** consisting of an UPy unit linked to a reactive isocyanate group. The electrophilic isocyanate can react with common nucleophilic end groups of telechelic polymers as hydroxy or amine groups (Fig. 1). To show the versatility of this approach OH telechelic poly(ethylene/butylene) was functionalized with **1** because it is almost completely amorphous and apolar, which increases the strength of the hydrogen bonds. Moreover, we will show that this concept is generally applicable to telechelic polyethers, polyesters, and polycarbonates, leading to a new set of supramolecular materials.

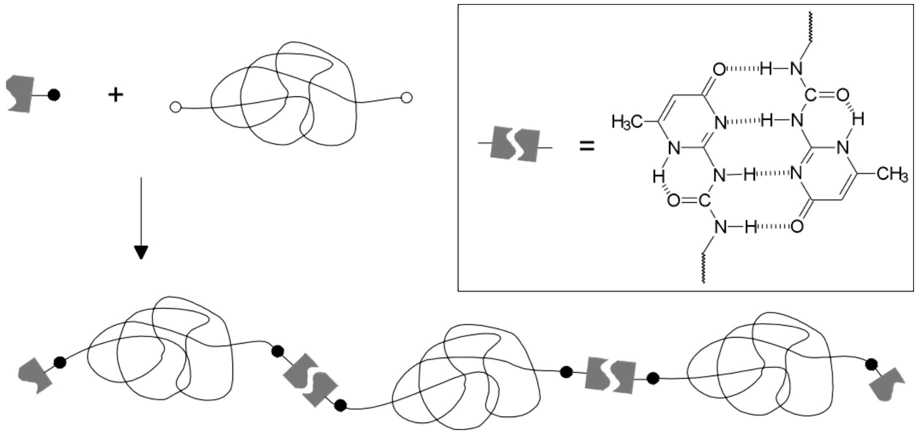
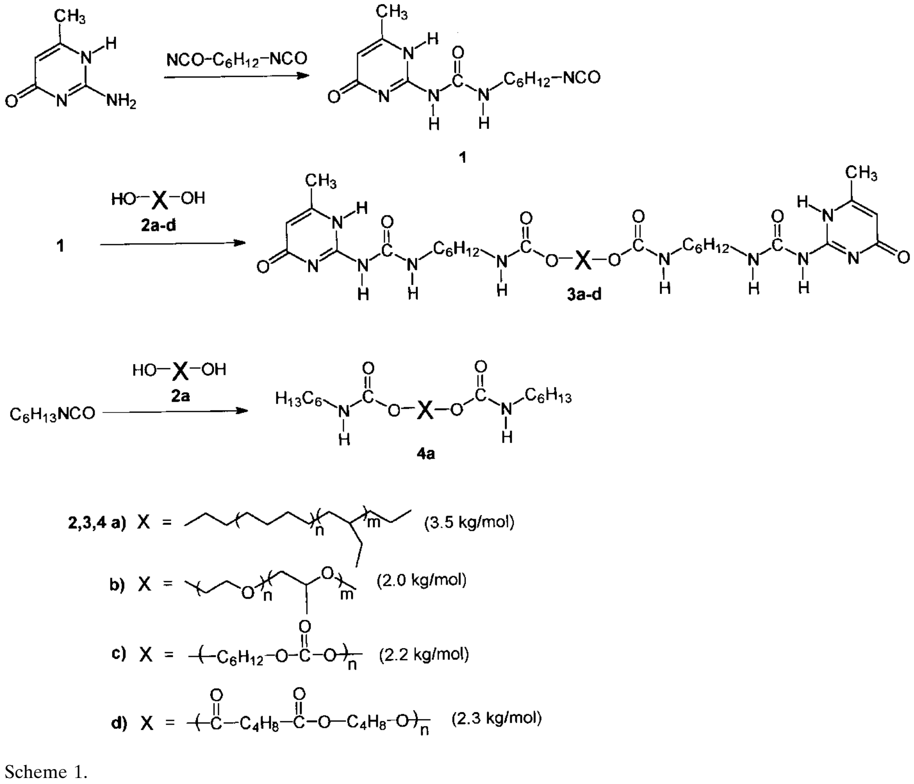


Fig. 1. Schematic drawing of functionalization of telechelic polymers with quadruple hydrogen-bonded ureido-pyrimidinone units.



Scheme 1.

Building block **1** (2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone) was prepared from 2-amino-4-hydroxy-6-methylpyrimidine using a six-fold excess of 1,6-hexyldiisocyanate. When the conversion was complete, excess diisocyanate was recovered by distillation, and the product was isolated in a yield of 94 % at a scale of 200 g. Polymers **3** were prepared by refluxing dilute solutions (30 mM) of hydroxy telechelic polymers **2** in chloroform with a two-fold excess of building block **1**, together with a small amount of dibutyltindilaurate as a catalyst. The conversion was determined with ^{1}H NMR spectroscopy, and after 10–16 h functionalization was complete (Scheme 1). Polymers **3** were obtained after a simple work-up procedure. Most of the excess of **1** in the polymer solution was removed by filtration, and residual **1** was removed by reacting it with silica at 60 °C for 1 h with the aid of a small amount of dibutyltindilaurate, followed by filtering off the silica-bound reactant. Due to the moderate solubility of **1** in chloroform the reaction time necessary for complete functionalization was 16 h at reflux temperature. This could be reduced to 1.5 h by using 10 % dimethyl sulfoxide (DMSO) in chloroform as solvent.

Functionalization of **2a** with **1** resulted in a dramatic change in materials properties. Whereas **2a**, having hydroxy end groups, is a viscous liquid (Fig. 2a), polymer **3a** with hydrogen-bonded units is an elastic solid (Fig. 2b). After dissolving functionalized polymer **3a** in chloroform a highly viscous solution was obtained. Addition of a small amount of trifluoroacetic acid (TFA), a solvent that breaks the hydrogen bonds, resulted in a substantial decrease in the viscosity, showing the reversibility of the chain extension. Moreover, when polymer **2a** was reacted with hexylisocyanate, the materials properties of the resulting polymer **4a** resembled those of the starting material **2a**. So the change in properties by functionalization with **1** is solely due to the association of the UPy end groups. Functionalization of polyether **2b**, polycarbonate **2c**, and polyester **2d** also led to a distinct improvement of materials properties; however, in the current paper we will focus on the properties of functionalized poly(ethylene/butylene) **3a**.

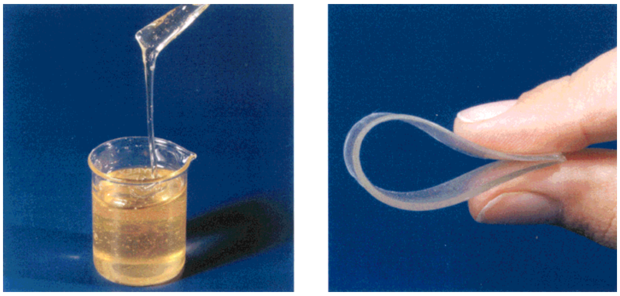


Fig. 2. Poly(ethylene/butylene) with OH end groups **2a** (left), poly(ethylene/butylene) functionalized with hydrogen-bonded units **3a** (right).

The thermal properties of **3a** were determined with dynamic mechanical thermal analysis (DMTA) (Fig. 3) and differential scanning calorimetry (DSC) (Fig. 4) and were compared with the properties of **2a** and **4a**, respectively.

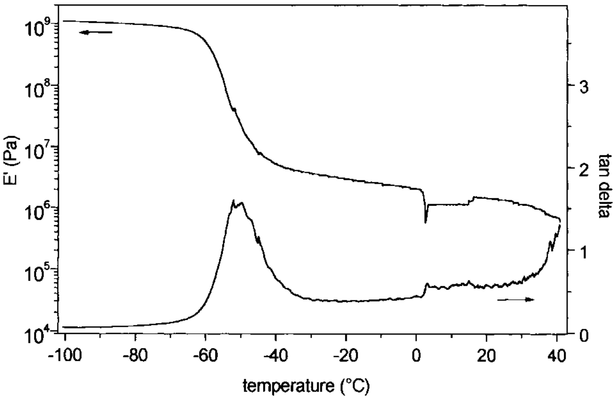


Fig. 3. DMTA curves of **3a**.

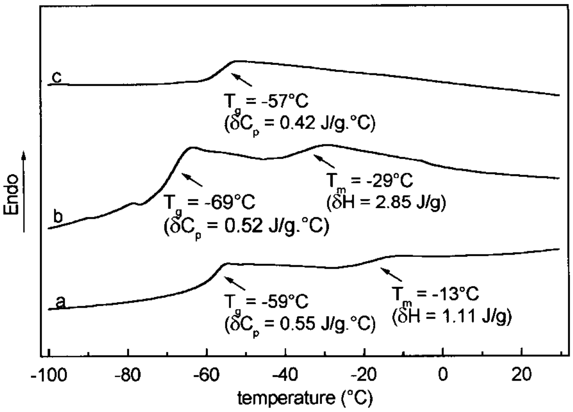


Fig. 4. DSC curves of: a) **2a**, b) **4a**, c) **3a** at a heating rate of 20 °C min^{-1}.

With DMTA at 1 Hz, a distinct glass transition at –50 °C was observed, while between –50 °C and room temperature, a rubber plateau at 5×10^6 Pa was discernible, indicating that the "virtual" molecular weight of the reversible polymer is extremely high. Obviously, at room temperature the material exhibits the characteristics of a soft rubber. The remarkable improvement of the properties suggests that, in addition to hydrogen bonding within the polymer chain, interchain interactions such as physical crosslinks are present. However, the transparent appearance of the material indicates that large clusters of hydrogen-bonded units are absent. DSC at a scanning rate of 20 °C/min revealed the glass transition (T_g) of polymer **3a** at –57 °C. This is comparable to the T_g of polymer **2a** at –59 °C and the T_g of **4a** at –69 °C. In addition to the glass transition, a small endotherm at –13 °C for **2a** and at –29 °C for **4a** was observed. Although polymer **2a** is a random copolymer (it is obtained by hydrogenation of polybutadiene containing a random distribution of 50 % 1,2-polymerized and 50 % 1,4-polymerized butadiene), there is still a tendency to form crystalline regions. In reversible polymer **3a** this tendency is almost absent due to the increase of the "virtual" molecular weight, which in turn leads to a decrease in diffusional freedom, preventing the formation of crystalline regions. The absence of a new melt endotherm in polymer **3a** indicates that the hydrogen-bonded units do not form large crystalline clusters themselves.

Dynamic oscillatory shear measurements were performed on polymers **2a** and **3a**. Figure 5 shows the master curves of the storage (G') and loss modulus (G'') as well as the dynamic viscosity (η^*) of both **2a** and **3a** at 40 °C. Polymer **3a** shows pronounced viscoelastic behavior; the moduli and viscosity exhibit strong frequency-dependent behavior. At low frequencies ($\omega \rightarrow 0$) the zero shear viscosity is determined at 2×10^6 Pa s. At higher frequencies the viscosity is frequency dependent with a slope of –1. Moreover, polymer **3a** shows a broad rubber plateau with a storage modulus of about 10^6 Pa at high frequencies. At lower frequen-

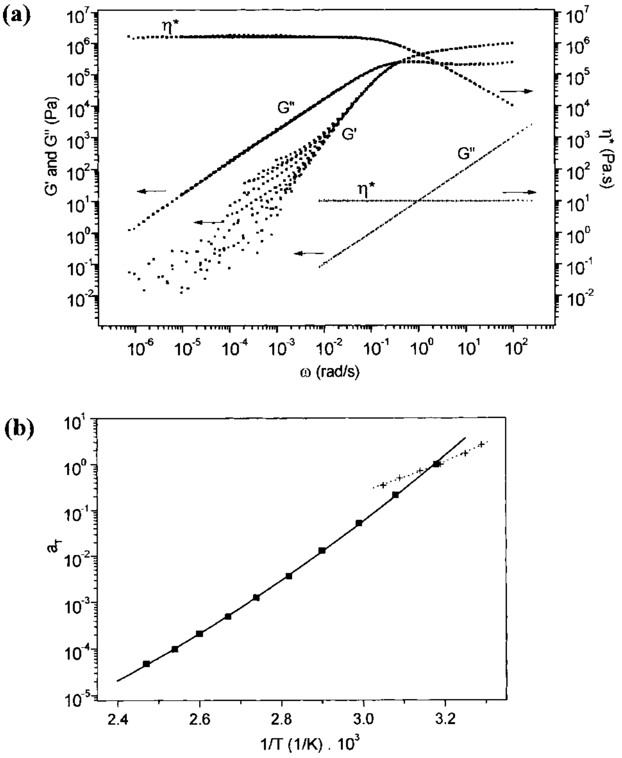


Fig. 5. a) Master curves of dynamic melt viscosity (η^*), storage (G') and loss (G'') moduli of **3a** (■) and η^* and G'' of **2a** (+) at 40 °C. b) Shift factors a_T as a function of T^{-1} for **3a** (■) and **2a** (+).

cies a sharp viscoelastic transition towards the terminal regime is observed. In the terminal regime the storage modulus (G') is proportional to the square frequency and the loss modulus (G'') is proportional to the frequency. In contrast to this, polymer **2a** has a low viscosity of 1×10^1 Pa s at 40 °C, and the viscosity shows no frequency dependence at high frequencies. Moreover, the loss modulus is proportional to the frequency over the complete frequency range, and a viscoelastic transition is not observed, which is typical for low-molecular-weight liquids.[8]

The failure of time–temperature superposition (TTS) at low frequencies, accompanied by a plateau in the storage modulus of polymer **3a**, is remarkable. According to theory this thermorheologically complex behavior can be caused by the reversibility of the association of the hydrogen-bonded units.[9] However, the presence of a plateau and the failure of TTS can also be an indication that small clusters of hydrogen-bonded units are present. Because the clusters are large relative to a single hydrogen-bonded dimer, the characteristic lifetime of these clusters is long (at low frequencies). The clusters act as physical crosslinks, like hard domains in thermoplastic elastomers (TPE) or the domains in side-chain liquid-crystalline polymers.[10]

Despite the failure of TTS, shifting of G'' data resulted in the determination of C_1 and C_2 parameters of the WLF (Williams, Landel, and Ferry) equation.[8] For polymer **2a**, $C_1 = 2.08$ and $C_2 = 59.21$ K. These values and the product C_1C_2 (= 123.16 K) are in good agreement with universal values of conventional macromolecules. For polymer **3a**, however, $C_1 = 13.86$ and $C_2 = 194.87$ K ($C_1C_2 = 2.70 \times 10^3$ K). The values of C_1 and C_2 of the WLF equation can be converted to an apparent activation energy for viscoelastic relaxation,[8] so the substantial difference in C_1 and C_2 between conventional and associating polymers indicates a higher apparent activation energy for associating polymer **3a**, showing the strong temperature dependency of **3a**. Large changes in C_1 and C_2 values have also been observed by Stadler et al. upon functionalization of polybutadiene with phenylurazole units.[4b]

In contrast to conventional high-molecular-weight polymers, reversible polymers with a high “virtual” molecular weight show excellent processability due to the strong temperature dependency of the melt viscosity (Fig. 6). The zero shear melt viscosity (η_0) of **3a** at 40 °C is 2×10^6 Pa s, while that of **2a** at 40 °C is 1×10^1 Pa s. Increasing the temperature by 10 °C gives rise to a drop in the viscosity of **3a** by a factor of 4, to 0.4×10^6 Pa s, while the same increase in temperature for **2a** results in a drop of only 5 Pa s (by a factor of 2); this important advantage of reversible polymers is illustrated in a plot of the zero shear viscosity versus the temperature (Fig. 6b).

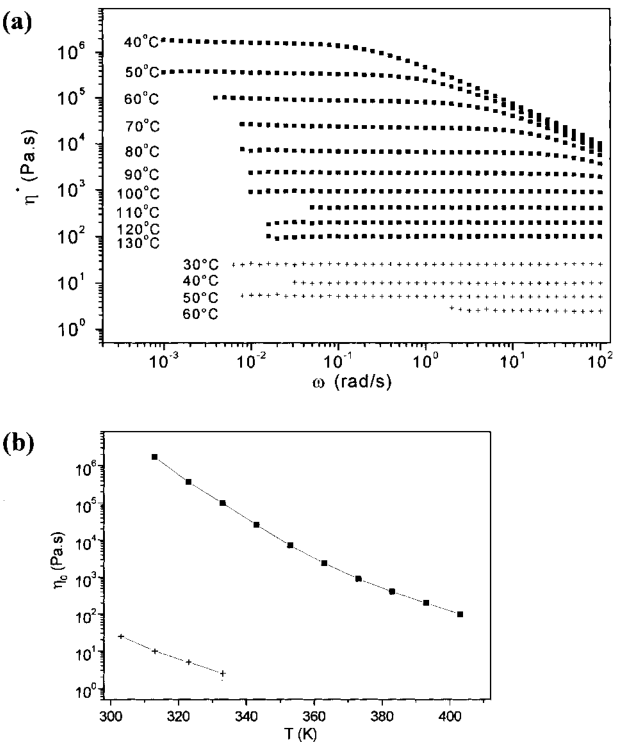


Fig. 6. a) Dynamic melt viscosity at different temperatures of **3a** (■) and **2a** (+). b) Zero shear viscosity as a function of T.

In conclusion, materials combining the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds are now within reach. The work presented here aims at closing the gap between polymers and oligomers by taking the best of both worlds. The ready availability of the starting compounds, the straightforward synthetic methodology for functionalizing the telechelic polymers, and the easy work-up procedure makes this strategy applicable for general use on an industrial scale. Further research will show the feasibility and limitations of this strategy. In the future, we will apply this general concept to π-conjugated oligomers, to obtain highly processable functional supramolecular polymers.

Experimental

Synthesis: Synthesis of 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone **1** was carried out according to the following procedure: A solution of 0.70 mol 2-amino-4-hydroxy-6-methylpyrimidine in 4.75 mol hexyldiisocyanate was heated at 100 °C for 16 h. Pentane was added and the resulting precipitate was filtered and washed with pentane. The white powder was dried at 50 °C under reduced pressure. The excess of hexyldiisocyanate was recovered by distillation. Yield: 94 %. m.p. 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.1 (s, 1H, $CH_3CN\underline{H}$), 11.9 (s, 1H, $CH_2NH(C{=}O)N\underline{H}$), 10.2 (s, 1H, $CH_2N\underline{H}(C{=}O)NH$), 5.8 (s, 1H, $C\underline{H}{=}CCH_3$), 3.3 (m, 4H, $NH(C{=}O)NHC\underline{H}_2 + C\underline{H}_2NCO$), 2.2 (s, 3H, $C\underline{H}_3C{=}CH$), 1.6 (m, 4H, $NCH_2C\underline{H}_2$), 1.4 (m, 4H, $CH_2CH_2C\underline{H}_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 156.3, 154.4, 148.1, 121.6, 106.4, 42.6, 39.5, 30.9, 29.1, 26.0, 25.9, 18.7. IR (KBr): ν 1675, 1701, 2279, 3233, 3466 cm^{-1}. Anal. Calcd. for $C_{13}H_{19}N_5O_3$: C, 53.23; H, 6.53; N, 23.88. Found: C, 53.37; H, 6.27; N, 23.77.

Polymers **3a–d** were prepared by the following procedure. To a solution of 15 mmol polymer **2** in 500 mL chloroform (dried over molecular sieves), 60 mmol 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone was added. After addition of 2 drops of dibutyltindilaurate the resulting solution was stirred at 60 °C for 16 h. The completeness of the reaction was checked with ^{1}H NMR. 500 mL chloroform was added and the solution was filtered. After concentrating the solution back to 500 mL, 5 g of silica (Merck Kieselgel 60) and 1 drop of dibutyltindilaurate were added, and the mixture was heated at 60 °C for 1 h. The silica was removed by filtration and the chloroform was removed in vacuo. The resulting material was dried for 2 days at 50 °C under reduced pressure. The absence of **1** in the material was checked by IR It is not necessary to remove the trace amounts of catalyst; however, precipitation of polymers **3a–d** from chloroform in methanol yields pure polymer. **3a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.1 (s, 2H, $CH_3CN\underline{H}$), 11.9 (s, 2H, $CH_2NH(C{=}O)N\underline{H}$), 10.1 (s, 2H, $CH_2N\underline{H}(C{=}O)NH$), 5.8 (s, 2H, $C\underline{H}{=}CCH_3$), 4.9 + 4.6 (s, 2H, $N\underline{H}(C{=}O)O$), 4.1 + 3.8 (m, 4H, $C\underline{H}_2O(C{=}O)NH$), 3.3 (m, 4H, $C\underline{H}_2NH(C{=}O)NH$), 3.2 (m, 4H, $C\underline{H}_2NH(C{=}O)O$), 2.2 (s, 6H, $C\underline{H}_3C{=}CH$), 1.6–1.1 (m, 414H, $CH_2C\underline{H}_2CH_2$), 0.8 (m, 190H, $CH_2C\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.36, 157.21, 157.01, 156.80, 154.94, 148.47, 106.93, 73.04, 63.59, 39.31, 39.09, 38.59, 38.09, 36.32, 33.65, 33.45, 30.88, 30.43, 29.98, 29.59, 27.00, 26.82, 26.66, 26.49, 26.34, 26.26, 26.10, 24.44, 19.17, 11.11, 10.87, 10.59. DSC (scanning rate 20 °C/min): $T_g = -57$ °C ($\Delta C_p = 0.4$ J/g °C).

Characterization: Differential scanning calorimetry: Thermal transitions of polymers **2** and **3** were determined on a Perkin Elmer Pyris 1 under a nitrogen atmosphere with heating and cooling rates of 20 °C min^{-1}. Dynamic mechanical thermal analysis: The sub-T_g dynamic mechanical spectra were recorded on a Perkin Elmer DMA 7 dynamic mechanical analyzer, calibrated with mercury and indium. A small rectangular bar of the polymer, size approximately 2 mm × 4 mm × 20 mm was subjected to a sinusoidal deformation at constant frequency, using the three point bending method. Measurements were carried out at a frequency of 1 Hz and a heating rate of 2 °C min^{-1}. The amplitude of the sinusoidal deformation was kept the same (25 μm) and the static force was always 10 % more then the dynamic force in order to ensure good contact between sample and probe. Dynamic oscillatory shear measurements: Dynamic mechanical measurements were performed on a Rheometrics RMS 800 in a cone–plate geometry (25 mm). Strain amplitudes up to 30 % were used, which are all well within the linear viscoelastic range.

Received: February 2, 2000
Final version: April 3, 2000

---

[1] a) K. C. Tam, R. D. Jenkins, M. A. Winnik, D. R. Basset, *Macromolecules* **1998**, *31*, 4149. b) K. C. Tam, M. L. Farmer, R. D. Jenkins, D. R. Basset, *J. Polym. Sci. B* **1998**, *36*, 2275. c) E. Alami, S. Abrahmsén-Alami, M. Vasilescu, M. Almgren, *J. Colloid Interface Sci.* **1997**, *193*, 152. d) S. Abrahmsén-Alami, P. Stilbs, *J. Colloid Interface Sci.* **1997**, *189*, 137. e) R. J. English, H. S. Gulat, R. D. Jenkins, S. A. Khan, *J. Rheol.* **1997**, *41*, 427.

[2] a) C. Chassenieux, R. Johannsson, D. Durand, T. Nicolai, P. Vanhoorne, R. Jérôme, *Colloids Surf.* **1996**, *112*, 155. b) A. Eisenberg, B. Hird, R. B. Moore, *Macromolecules* **1990**, *23*, 4098. c) E. P. Otocka, M. Y. Hellman, L. L. Blyler, *J. Appl. Phys.* **1969**, *40*, 4221.

[3] a) C. P. Lillya, R. J. Baker, S. Hütte, H. H. Winter, Y.-G. Lin, J. Shi, C. Dickinson, J. C. W. Chien, *Macromolecules* **1992**, *25*, 2076. b) S. Abed, S. Boileau, L. Bouteiller, N. Lacoudre, *Pol. Bull.* **1997**, *39*, 317.

[4] a) M. Müller, A. Dardin, U. Seidel, V. Balsamo, B. Iván, H. W. Spiess, R. Stadler, *Macromolecules* **1996**, *29*, 2577. b) M. Müller, U. Seidel, R. Stadler, *Polymer* **1995**, *36*, 3143. c) L. L. de Lucca Freitas, R. Stadler, *Colloid Polym. Sci.* **1988**, *266*, 1095. d) L. L. de Lucca Freitas, R. Stadler, *Macromolecules* **1987**, *20*, 2478. e) R. Stadler, L. L. de Lucca Freitas, *Colloid Polym. Sci.* **1986**, *264*, 773.

[5] a) F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 6761. b) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601.

[6] J. H. K. K. Hirschberg, F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma, E. W. Meijer, *Macromolecules* **1999**, *32*, 2696.

[7] R. F. M. Lange, M. van Gurp, E. W. Meijer, *J. Polym. Sci.* **1999**, *37*, 3657.

[8] J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York **1980**.

[9] a) M. E. Cates, *J. Phys. Chem.* **1990**, *94*, 371. b) L. Leibler, M. Rubinstein, R. H. Colby, *Macromolecules* **1991**, *24*, 4701.

[10] M. E. De Rosa, W. W. Adams, T. J. Bunning, H. Shi, S. H. Chen, *Macromolecules* **1996**, *29*, 5650. b) S. Ahuja, M. L. Tsai, S. H. Chen, *Polym. Mater. Sci. Eng.* **1988**, *58*, 1034. c) T. Yamaguchi, T. Asada, *Polym. Bull.* **1991**, *25*, 611.

Nanocrystalline Nickel Nanoparticles[**]

By *Michael P. Zach* and *Reginald M. Penner*[*]

We describe a new electrochemical technique—the "H_2 coevolution method"—for electrodepositing nickel particles ranging in diameter from 20 to 600 nm on graphite surfaces. The H_2 coevolution method enabled the size-selective deposition of nickel nanoparticles that are very narrowly dispersed in diameter. Specifically, a relative standard deviation of the diameter, $RSD_{dia.}$, of 8–15 % was routinely obtainable over the entire particle diameter range indicated above. In this particle size regime,[1] this degree of size monodispersity is comparable to the best that has been obtained for the growth of nickel particles in solution.[2] In addition to size monodispersity, the nickel particles produced by H_2 coevolution are nanocrystalline: each nanoparticle produced by this method is a nanocrystalline

---

[*] Prof. R. M. Penner, M. P. Zach
Institute for Surface and Interface Science
Department of Chemistry
University of California, Irvine
Irvine, CA 92679-2025 (USA)
E-mail: rmpenner@uci.edu

[**] This work was funded by the National Science Foundation (#DMR-9876479) and the Petroleum Research Fund of the American Chemical Society (#33751-AC5). The authors also gratefully acknowledge the financial support of the A. P. Sloan Foundation Fellowship, and the Camille and Henry Dreyfus Foundation. Finally, donations of graphite by Dr. Art Moore of Advanced Ceramics are gratefully acknowledged.