Polymerization-Induced Phase Separation Using Hydrogen-Bonded Supramolecular Polymers

Henk M. Keizer,[†] Rint P. Sijbesma,*[,†] Johan F. G. A. Jansen,[‡] George Pasternack,[§] and E. W. Meijer*[,†]

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5300 MB, Eindhoven; DSM Research, Section RP-CT, P.O. Box 18, 6160 MD, Geleen, The Netherlands; and DSM Desotech Inc., 1122 St. Charles Street, Elgin, Illinois 60120

Received March 5, 2003; Revised Manuscript Received May 9, 2003

ABSTRACT: The concept of polymerization-induced phase separation with hydrogen-bonded supramolecular polymers was investigated by the photopolymerization of films containing mixtures of supramolecular polymer **1a** or **1b** and varying amounts of monoacrylate and diacrylate with UV-A (320−400 nm) radiation (5 W/cm^2) for 0.3 s. The extent of the phase separation after photopolymerization was determined by differential scanning calorimetry and scanning electron microscopy, which showed that film 1 containing no diacrylate is macrophase-separated, while films 2 and 3 containing 17.0 or 42.5% diacrylate are microphase-separated. Increasing the amount of diacrylates has a strong influence on the morphology development, as it decreases the length scale of the phase separation by shortening the time available before vitrification sets in—in this way decreasing the crystallinity of the supramolecular phase. Tensile tests and DMTA measurements showed that the mechanical properties of the films containing the hydrogen-bonded supramolecular polymers are comparable to those films containing covalent high molecular weight polymers.

Introduction

Supramolecular polymers are a relatively new class of polymers in which repeating units are connected by noncovalent interactions.[1] In the past decade, following the development of strong hydrogen-bonding dimers,[2−4] several research groups have applied these dimers for the formation of hydrogen-bonded supramolecular polymers.[5−9] Within our group, hydrogen-bonded supramolecular polymers were developed on the basis of the self-complementary quadruple hydrogen-bonding ureido-pyrimidinone group (Figure 1).[10−13] The high dimerization constant (6 × 10^7 M^{-1} in chloroform)[14,15] makes it possible to obtain materials with a high degree of polymerization.

It was shown that functionalization of telechelic oligomers with ureido-pyrimidinone groups results in a spectacular improvement of the material properties.[13] These and other supramolecular materials[16,17] show pronounced viscoelastic behavior, and because of the reversibility of the bonds between the repeat units, they respond to environmental changes. As a result, the viscosity in bulk and in solution highly depends on temperature and concentration.[11]

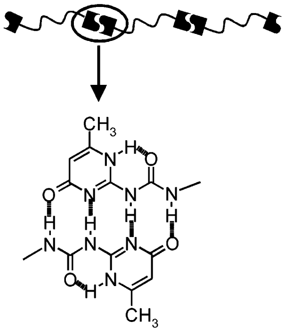


Figure 1. Self-complementary quadruple hydrogen-bonding ureido-pyrimidinone group in a supramolecular polymer.

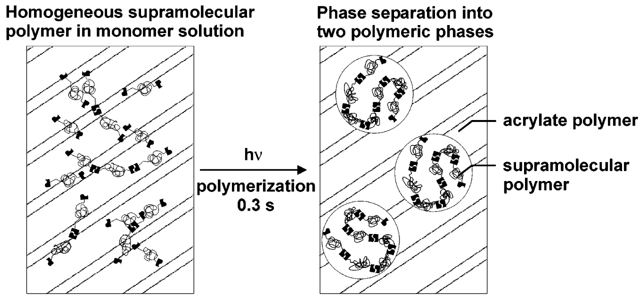


Figure 2. Schematic representation of PIPS using hydrogen-bonded supramolecular polymers.

One application where the reversibility of supramolecular polymers might be advantageous is in polymerization-induced phase separation (PIPS), as schematically shown in Figure 2.[18] In PIPS, a polymer is dissolved in a reactive monomer, which is subsequently polymerized to cause phase separation, resulting in two polymeric phases with certain morphology. PIPS is used to produce multiphase composite materials like polymeric dispersed liquid crystals (PDLCs)[19−21] and high impact polystyrene.[22] By using this principle in the production of polymeric materials, the use of solvent is avoided, and it is fast and clean.[23]

The rate of phase separation in PIPS is generally limited by the mobility of the dissolved polymer.[24−27] For conventional polymers, the most important mechanism for stress relaxation is reptation, described by de Gennes[28] and by Doi and Edwards.[29−32] Supramolecular polymers, however, can relax via the additional mech-

---

[†] Eindhoven University of Technology.

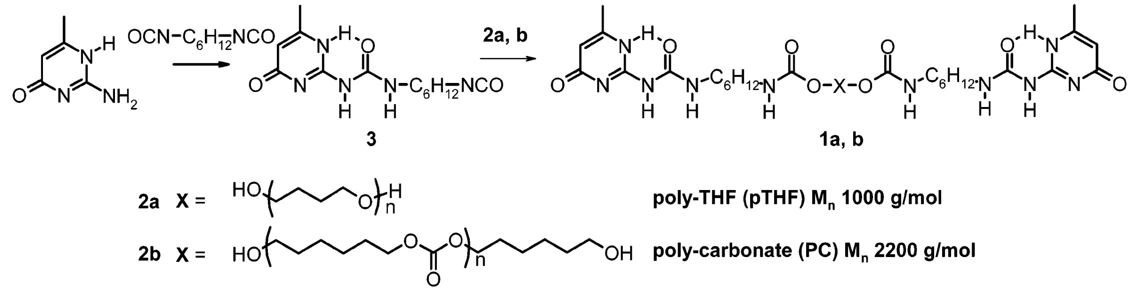
[‡] DSM-Research.

[§] DSM Desotech.

[*] Corresponding authors. E-mail: R.P.Sijbesma@tue.nl; E.W.Meijer@tue.nl.

10.1021/ma034284u CCC: $25.00

Scheme 1. Synthesis of Supramolecular Polymers 1a and 1b



anism of dissociation and association of the hydrogen bonds, a process theoretically described by Cates.[33,34] Indeed, we have shown that dissociation and association of the hydrogen bonds contribute to the stress relaxation of hydrogen-bonded supramolecular polymers.[13] This results in a strong dependency of the viscosity on the monomer concentration. Therefore, we anticipated that the use of a supramolecular polymer in the starting mixture of PIPS would allow a high degree of phase separation within a very short reaction time. Here we report on polymerization-induced phase separation of solutions of hydrogen-bonded supramolecular polymers in acrylates, within the short reaction times (0.3 s) used in UV-curing. This strategy could be used for either stratification or patterning via a mold in thin films.

Results and Discussion

The concept of PIPS with supramolecular polymers was investigated in mixtures with acrylate monomers, due to their ability to be photopolymerized in a very short time (0.3 s) by UV-curing. Supramolecular polymers **1a** and **1b** were synthesized on grounds of their synthetic accessibility and their anticipated high solubility in acrylate monomers (Scheme 1). The reported synthesis[13] of polymers **1a** and **1b** was improved by shortening the reaction time to 3 h in chloroform.

To study polymerization-induced phase separation, combinations of acrylates and supramolecular polymers **1a** and **1b** with high miscibility were identified prior to polymerization (Figure 3). Functionalized polyTHF **1a** was found to dissolve in polar acrylates like 2-hydroxyethyl acrylate (HEA) and phenoxyethoxy acrylate (PEA) up to high weight percentages of 50%. Polycarbonate **1b** dissolves up to 25 wt % in more apolar acrylates like isobutyl acrylate (iBA). Clear solutions of the supramolecular polymers were obtained by heating the mixtures for several hours at 80 °C. The solutions remained clear after cooling to room temperature.

Films containing either supramolecular polymer **1a** or **1b** and varying amounts of monoacrylate and diacrylate were prepared by exposing a 100 μm thick film of the mixture to UV-A (320−400 nm) radiation (5 W/cm^2) for 0.3 s under a nitrogen atmosphere at room temperature (Table 1). For comparison, films containing polymerizable urethane acrylates (UA) (Figure 3) or random copolymer MMA/EA (acryloid) were prepared (vide infra).

After UV-curing the films were colorless, transparent, flexible, and strong enough to be pealed off the glass substrate. Film 4 containing no diacrylate was an exception because it was opaque and too soft to be easily pealed off the glass substrate. With an optical microscope, it was determined that film 4 has a morphology of small droplets (~2 μm) of **1b** in a continuous matrix of isobutyl acrylate. To characterize the morphology of the films, scanning electron microscopy (SEM) measurements were performed (Figure 4). For the SEM measurements supramolecular polymer **1b** was (partially) etched out of films 4−6 by immersion of the films for 10 min in chloroform and drying in air afterward. The SEM micrographs in Figure 4 show that in films 4−6 the supramolecular phase as the minor phase is dispersed as small droplets in a continuous matrix of the acrylate phase. The size of the droplets containing supramolecular polymer clearly decreases with increas-

Table 1. Composition of UV-Polymerized Films 1−8

film	polymer	wt %	monoacrylate	wt %	diacrylate	wt %
1	**1a**	30	PEA	60	TEGDA	10
2	**1a**	15	HEA	72.5	HDDA	12.5
3	**1a**	25	HEA	64	HDDA	11
4	**1b**	10	iBA	90	HDDA	0
5	**1b**	15	iBA	68	HDDA	17
6	**1b**	15	iBA	42.5	HDDA	42.5
7	UA	30	PEA	60	TEGDA	10
8	acryloid	30	PEA	60	TEGDA	10

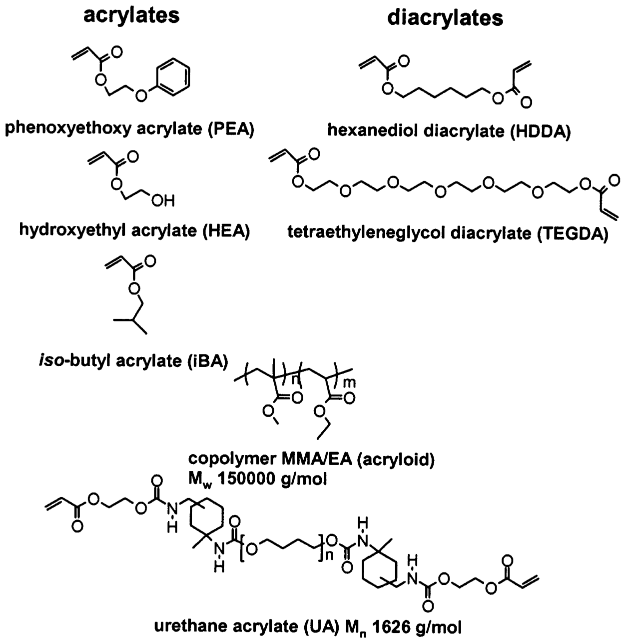


Figure 3. Structures of monoacrylates, diacrylates, random copolymer MMA/EA (acryloid), and urethane acrylate (UA).

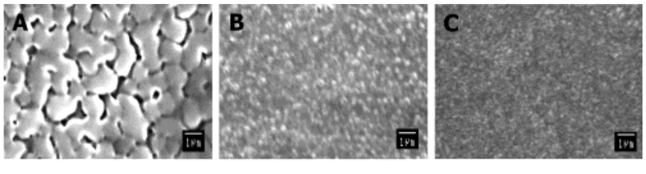


Figure 4. SEM micrographs of (A) film 4, (B) film 5, and (C) film 6 after etching with chloroform.

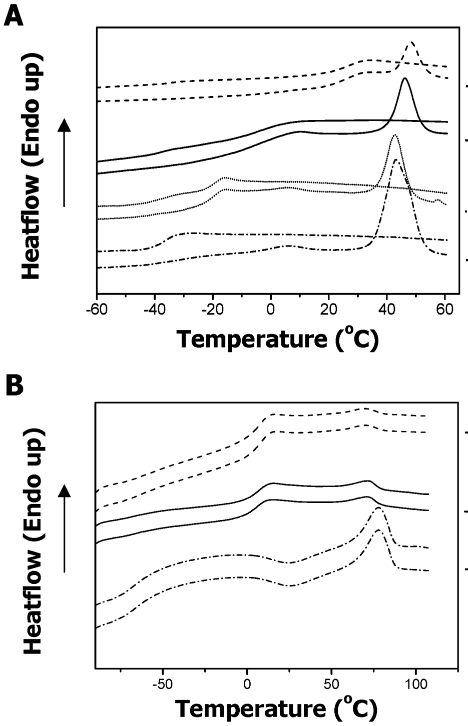


Figure 5. DSC thermograms of (A) first and second heating runs of films 4−6 and pure **1b** and (B) first and second heating runs of films 2, 3, and pure **1a**.

ing amounts of diacrylate from ~2 μm, to ~200 nm, to <100 nm in films 4, 5, and 6, respectively. This observation can be explained by the higher rate of reaction of diacrylates compared to monoacrylates, which causes an earlier onset of gelation and earlier vitrification.[35] Moreover, the length scale on which phase separation takes place is influenced by the time available for diffusion of the supramolecular phase before it is trapped in the acrylate network. Thus, the increasing amount of diacrylates decreases the length scale of the phase separation by shortening the time available before vitrification sets in.

Further investigation of the extent of phase separation for films 2−6 was performed by differential scanning calorimetry (DSC). In the thermograms (Figure 5) the second heating runs contain both the T_g's of the acrylate phase and the supramolecular phase, and in the first heating runs a melting peak of the supramolecular phase is observed in all films. These melting points are similar to those of materials **1a** and **1b** with T_m 74.5 and 42.8 °C, respectively. Therefore, it can be concluded that film 5, which contains no diacrylates, is macrophase-separated, while films 5 and 6 containing 17.0 and 42.5% diacrylate, respectively, are microphase-separated.

When the areas (ΔH) below the melting peak around 45 °C are compared ($\Delta H = 2.7$, 6.5, 8.0, and 32.9 J/g for films 6, 5, 4, and **1b**, respectively), it is clear that the crystallinity of the supramolecular **1b** phase decreases with increasing amount of diacrylates. The decrease in the crystallinity of the supramolecular polymer phase with increasing amounts of diacrylates confirms the observations with SEM (vide supra) that the length scale of phase separation is influenced by the amount of diacrylate.

The mechanical properties of films 1, 7, and 8 were studied. Films 7 and 8 contain a reactive urethane acrylate (UA) oligomer with the same molecular weight as **1a** or a high molecular weight acrylate copolymer (Acryloid), respectively. The mechanical properties of the three films were measured with dynamic mechanical thermal analysis (DMTA) and tensile tests; for the results see Table 3. A typical DMTA curve is shown in Figure 6.

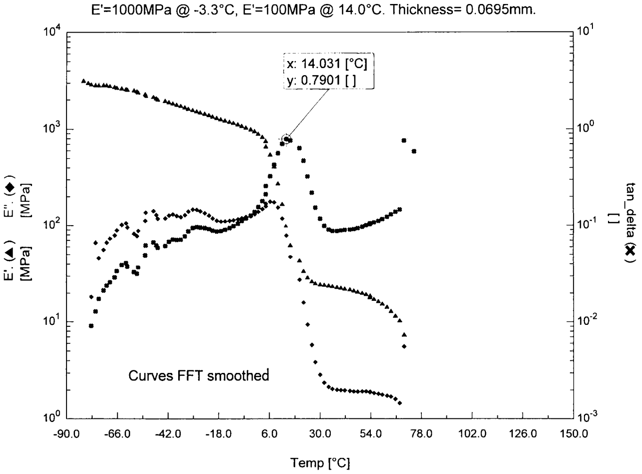


Figure 6. DMTA curves of film 1 containing **1a** measured at 1 Hz.

Table 2. DSC Results for Cured Films 2−6

	acrylate phase		supramolecular phase	
film	first heating run	second heating run	first heating run	second heating run
2	T_g 6.2 °C	T_g 6.2 °C	T_g −62.2 °C	T_g −62.2 °C
			T_m 71.7 °C	T_m 71.7 °C
3	T_g 6.9 °C	T_g 6.9 °C	T_g −62.2 °C	T_g −62.2 °C
			T_m 69.5 °C	T_m 69.5 °C
4	T_g −20.3 °C	T_g −20.8 °C	T_m 42.8, 6.1 °C	T_g −33.3 °C
5	T_g −1.5 °C	T_g −1.5 °C	T_m 46.2 °C	T_g −37.0 °C
6	T_g 25.9 °C	T_g 25.9 °C	T_m 48.3 °C	T_g −33.8 °C

Table 3. DMTA and Tensile Tests on Cured Films 1, 7, and 8

	tensile tests			DMTA	
film	elongation at break (%)	tensile strength (MPa)	Young's modulus (MPa)	T_g/tan δ (°C)	E_0 (MPa)
1	30.2	2.27	17.8	11.5	1.7
7	38.8	1.61	5.73	11.0	7.1
8	69.1	1.74	9.03	15/30	2.0

From the mechanical tests, it can be concluded that films 1, 7, and 8 all have good mechanical properties despite the difference in the composition of the films. This shows that the hydrogen-bonded supramolecular polymer **1a** in film 6 behaves as a high molecular weight polymer and does not act as a low molecular weight softener, which would reduce the modulus. As expected, film 7 is not phase-separated due to the reactive end groups of the oligomers, which forms a network with acrylate phase, and this increase in cross-link density explains also the somewhat higher E_0 of film 7.

Conclusions

In summary, we have shown that the use of supramolecular polymers allows polymerization-induced phase separation (PIPS) with very short reaction times. Two separated polymer phases are formed simultaneously by performing a simple polymerization. Increasing the amount of diacrylates has a strong influence on the morphology development, as it decreases the length scale of the phase separation by shortening the time available before vitrification sets in—in this way decreasing the crystallinity of the supramolecular phase. The mechanical properties of the films containing the supramolecular polymer are comparable to those films containing covalent high molecular weight polymers.

A study of the morphology development during PIPS has started where we are focusing on influence of the dynamic behavior of the supramolecular polymer toward the environment on the rate of phase separation and coarsening. For applications, it would be interesting to look at the possibility of self-stratification in films containing supramolecular polymers using PIPS. Although the formation of two polymeric phases in one polymerization step is advantageous, it also complicates the study of the morphology development because the phase-separation process is influenced by both the radical polymerization of the reactive solvent and the supramolecular polymerization.

Experimental Section

Synthesis of α,*ω*-Functionalized PolyTHF (1a). To a solution of polyTHF (**2a**) (20 g, 0.020 mol) in chloroform (150 mL), synthon (**3**)[13] (12.31 g, 0.042 mol) and dibutyltin dilaurate (2 drops) were added. The mixture was refluxed for 3 h, resulting in a suspension. The suspension was filtered, and to the filtrate, silica and dibutyltin dilaurate (2 drops) were added. This mixture was refluxed overnight, after which the silica was filtered off. The solvent in the filtrate was removed under vacuum, and the remaining solid (white powder) was precipitated out of acetone (30 g, 95%). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 13.1 (s, 1H, $\mathrm{CH_3{-}C{-}N}H$), 11.9 (s, 1H, $\mathrm{CH_2{-}O{-}(C{=}O){-}N}H$), 10.1 (s, 1H, $\mathrm{CH_2{-}N}H\mathrm{{-}(C{=}O){-}NH}$), 5.8 (s, 2H, $\mathrm{C}H\mathrm{{=}C{-}CH_3}$), 4.9 + 4.6 (s, 2H, $\mathrm{N}H\mathrm{{-}(C{=}O){-}O}$), 4.1 (m, 4H, $\mathrm{C}H_2\mathrm{{-}O{-}(C{=}O){-}NH}$), 3.4 (m, 64H, $\mathrm{C}H_2\mathrm{{-}O{-}CH_2}$), 3.3 (m, 4H, $\mathrm{C}H_2\mathrm{{-}NH{-}(C{=}O){-}O}$), 3.2 (m, 4H, $\mathrm{C}H_2\mathrm{{-}NH{-}(C{=}O){-}NH}$), 2.2 (s, 6H, $\mathrm{C}H_3\mathrm{{-}CH{=}C}$), 1.6 (m, 68H, $\mathrm{O{-}CH_2{-}C}H_2 + \mathrm{N{-}CH_2{-}C}H_2$), 1.4 (m, 4H, $\mathrm{CH_2{-}CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 298 K): δ 173.36, 156.78, 154.92, 148.49, 106.89, 70.88, 70.82, 70.46, 64.70, 40.88, 39.84, 29.98, 29.54, 26.71, 26.43, 26.32, 26.15, 19.14. DSC (scanning rate 20 °C/min): $T_\mathrm{m} = 77.93$ °C ($\Delta H = 12.6$ J/(g °C)); $T_\mathrm{g} = -63.78$ °C ($\Delta C_p = 0.38$ J/(g °C)).

Synthesis of α,*ω*-Functionalized Polycarbonate (1b). To a solution of polycarbonate (**2b**) (9 g, 4.46 mmol) in chloroform (80 mL), synthon (**3**)[13] (3.0 g, 10.2 mmol) and dibutyltin dilaurate (2 drops) were added. The mixture was refluxed during overnight, resulting in a suspension. The suspension was filtered, and to the filtrate, silica and dibutyltin dilaurate (2 drops) were added. This mixture was refluxed overnight, after which the silica was filtered off. The solvent in the filtrate was removed under vacuum, yielding a solid polymer film (9.9 g, 85%). ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 13.1 (s, 1H, $\mathrm{CH_3{-}C{-}N}H$), 11.9 (s, 1H, $\mathrm{CH_2{-}NH{-}(C{=}O){-}N}H$), 10.1 (s, 1H, $\mathrm{CH_2{-}N}H\mathrm{{-}(C{=}O){-}NH}$), 5.8 (s, 2H, $\mathrm{C}H\mathrm{{=}C{-}CH_3}$), 4.9 + 4.6 (s, 2H, $\mathrm{N}H\mathrm{{-}(C{=}O){-}O}$), 4.1−3.9 (m, 30H, $\mathrm{C}H_2\mathrm{{-}O{-}(C{=}O){-}O}$), 3.3 (m, 4H, $\mathrm{C}H_2\mathrm{{-}NH{-}(C{=}O){-}O}$), 3.2 (s, 1H, $\mathrm{C}H_2\mathrm{{-}NH{-}(C{=}O){-}NH}$), 2.2 (s, 6H, $\mathrm{C}H_3\mathrm{{-}CH{=}C}$), 1.6−1.7 (m, 34H, $\mathrm{C}H_2\mathrm{{-}CH_2{-}O{-}(C{=}O){-}O} + \mathrm{N{-}CH_2{-}C}H_2$), 1.5−1.4 (m, 34H, $\mathrm{CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_2{-}O{-}(C{=}O){-}O} + \mathrm{CH_2{-}CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 298 K): δ 173.31, 156.95, 156.74, 154.89, 148.48, 106.86, 70,79 (m), 64.67, 40.85, 39.95, 39.80, 29.96, 29.51, 26.70 (m), 19.14. DSC (scanning rate 20 °C/min): $T_\mathrm{m} = 43.1$ °C ($\Delta H = 32.9$ J/(g °C)), 5.6 °C ($\Delta H = 2.2$ J/(g °C)); $T_\mathrm{g} = -36.99$ °C ($\Delta C_p = 0.58$ J/(g °C)).

UV-Curing Procedure. A typical UV-curable solution consists of 25−30 wt % of hydrogen-bonded polymer, 60 wt % of monoacrylate, 10−15 wt % of diacrylate, and 1% of photoinitiator (Irgacure 907). In an oven, this solution is heated at 80 °C until it is homogeneous. Then a 100 μm film is (mechanically) drawn on a glass substrate and UV-cured under nitrogen with a Fusion F600 D-Bulb ($I_0 = 5$ W/cm^2) with a belt speed of 10.4 m/min, which is equivalent to an irradiation time of 0.3 s.

Characterization. The differential scanning calorimetry thermograms for films 1−3, 7, and 8 and polymers **1a** and **1b** were recorded on a Perkin-Elmer Pyris-1 under a nitrogen atmosphere with heating and cooling rates of 20 °C min^{-1}. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or a Bruker AC 400 with TMS as internal reference. SEM studies on gold-sputtered samples were performed on a JEOL JSM-840A microscope at an acceleration voltage of 10 kV. Before the SEM measurements the samples were immersed for 10 min in chloroform, after which the samples were dried in the air overnight.

Acknowledgment. We gratefully thank STW for financial support. The management of DSM Research and DSM Desotech is kindly acknowledged for their permission to publish this work. Furthermore, we thank Qianyao Sun for performing the SEM measurements.

References and Notes

(1) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.
(2) Corbin, P. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 3779−3780.
(3) Zimmerman, S. C.; Murray, T. J. *Tetrahedron Lett.* **1994**, *35*, 4077−4080.
(4) Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092−9093.
(5) Kotera, M.; Lehn, J. M.; Vigneron, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 197−199.
(6) Fouquey, C.; Lehn, J. M.; Levelut, A. M. *Adv. Mater.* **1990**, *2*, 254−257.
(7) Griffin, A. C.; Lee, C. M.; St. Pourcain, C. B. *Polym. Mater. Sci. Eng.* **1995**, *72*, 172.
(8) Alexander, C.; Jariwala, C. P.; Lee, C. M.; Griffin, A. C. *Macromol. Symp.* **1994**, *77*, 283−294.
(9) Castellano, R. K.; Nuckolls, C.; Rebek, J., Jr. *Polym. News* **2000**, *25*, 44−52.
(10) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.
(11) Ky Hirschberg, J. H. K.; Beijer, F. H.; van Aert, H. A.; Magusin, P. C. M. M.; Sijbesma, R. P.; Meijer, E. W. *Macromolecules* **1999**, *32*, 2696−2705.
(12) Lange, R. F. M.; Van Gurp, M.; Meijer, E. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657−3670.
(13) 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.
(14) Söntjens, S. H. M.; Sijbesma, R. P.; van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487−7493.
(15) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761−6769.
(16) Rieth, L. R.; Eaton, R. F.; Coates, G. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 2153−2156.
(17) Castellano, R. K.; Clark, R.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 12418−12421.
(18) Doane, J. W.; Vaz, N. A.; Wu, B. G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269−271.
(19) Boots, H. M. J.; Kloosterboer, J. G.; Serbutoviez, C.; Touwslager, F. J. *Macromolecules* **1996**, *29*, 7683−7689.
(20) Serbutoviez, C.; Kloosterboer, J. G.; Boots, H. M. J.; Touwslager, F. J. *Macromolecules* **1996**, *29*, 7690−7698.
(21) Serbutoviez, C.; Kloosterboer, J. G.; Boots, H. M. J.; Paulissen, F. A. M. A.; Touwslager, F. J. *Liq. Cryst.* **1997**, *22*, 145−156.
(22) Fischer, M.; Hellmann, G. P. *Macromolecules* **1996**, *29*, 2498−2509.
(23) Nwabunma, D.; Chiu, H.-W.; Kyu, T. *Macromolecules* **2000**, *33*, 1416−1424.
(24) Rajaram, C. V.; Hudson, S. D.; Chien, L. C. *Chem. Mater.* **1996**, *8*, 2451−2460.
(25) Rajaram, C. V.; Hudson, S. D.; Chien, L. C. *Polymer* **1998**, *39*, 5315−5319.
(26) Maugey, J.; Van Nuland, T.; Navard, P. *Polymer* **2001**, *42*, 4353−4366.
(27) Okada, M.; Sakaguchi, T. *Macromolecules* **1999**, *32*, 4154−4156.

(28) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(29) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 38−54.

(30) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789−1801.

(31) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802−1817.

(32) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1818−1832.

(33) Cates, M. E. *Macromolecules* **1987**, *20*, 2289−2296.

(34) Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869−6892.

(35) O'Neil, G. A.; Wisnudel, M. B.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 7477−7490.

MA034284U