1054 *Macromolecules* **2004,** *37,* 1054−1061

Influence of Poly(ethylene oxide) Grafts on Kinetics of LCST Behavior in Aqueous Poly(*N*-vinylcaprolactam) Solutions and Networks Studied by Modulated Temperature DSC

Kurt Van Durme,[†] Sam Verbrugghe,[‡] Filip E. Du Prez,[‡] and Bruno Van Mele*,[†]

Department of Physical Chemistry and Polymer Science, FYSC (TW), Vrije Universiteit Brussel, Belgium, and Department of Organic Chemistry, Polymer Chemistry Division, Ghent University, Belgium

Received September 5, 2003; Revised Manuscript Received November 26, 2003

ABSTRACT: The (specific) heat capacity signal from modulated temperature DSC can be used to measure the onset of phase separation in aqueous poly(*N*-vinylcaprolactam) (PVCL) solutions, showing a type I LCST demixing behavior. Quasi-isothermal measurements through the phase transition show large excess contributions in the (apparent specific) heat capacity, caused by demixing and remixing heat effects on the time scale of the modulation. These excess contributions and their time-dependent evolution are useful to describe the kinetics of phase separation and to follow the related morphology development. Partial vitrification of the polymer-rich phase and a higher polymer concentration in the solutions lower the rate of phase separation. The introduction of hydrophilic poly(ethylene oxide) grafts onto PVCL lowers the demixing temperatures and markedly enhances the rate of phase separation, for both aqueous PVCL solutions and PVCL hydrogels.

Introduction

Some low-temperature polymer/water solutions phase-separate when the temperature is raised above a certain temperature, which is often characterized by the cloud point temperature (T_{CP}). Hence, a lower critical solution temperature (LCST) type of demixing behavior is found. The LCST is the lowest possible T_{CP} in a temperature/composition phase diagram of a certain polymer/water system. Such water-soluble polymers attract a lot of attention due to a wide range of potential applications.[1] Information on the rate of change from a homogeneous to a heterogeneous system and vice versa is of importance to design applications. Little is known, however, about the kinetics of phase separation and morphology development in these polymer/water systems.[2] Swelling and shrinking of membranes based on thermoresponsive polymers, for example, is usually studied by "ex-situ" gravimetric analysis.[3]

A well-known polymer of this kind is poly(*N*-vinylcaprolactam) (PVCL), showing a dissolution/precipitation transition in water at temperatures close to physiological temperatures, which opens perspectives for applications in biochemistry and medicine.[4,5] When PVCL is incorporated into a polymer network, the network will swell in cold water and deswell while heating beyond T_{CP}. A high shrinking rate of these thermoresponsive hydrogels is quite important as for most applications an abrupt deswelling is needed. A common problem is the formation of a dense hydrophobic shell at the surface. This diminishes the diffusion of water out of the gel particle.

Two methods have been reported to solve this problem: Yan et al. synthesized a macroporous poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel above T_{CP}, causing a rapid deswelling.[6] Another method is the incorporation of water channels in the hydrogel, thereby accelerating the water diffusion. For example, Okano et al. prepared quickly shrinking hydrogels by grafting hydrophilic poly(ethylene oxide) (PEO) onto a PNIPAAm network.[7] The free mobile ends of the grafts enhance water diffusion. The latter strategy is followed in this work to enhance the deswelling/reswelling kinetics of PVCL-based polymer systems. PEO grafts are incorporated in PVCL gels by making use of the macromonomer method. In previous work, the phase separation of PVCL and of related graft copolymers and segmented polymer networks has been investigated by DSC, turbidimetry, and scattering techniques.[8−11]

In this study, modulated temperature differential scanning calorimetry (MTDSC) will be used to evaluate the demixing kinetics of the PEO-grafted PVCL-based hydrogels as a function of the number of PEO grafts. For comparison, PVCL-*graft*-PEO copolymers will be investigated, too.

In the study of polymeric materials by means of MTDSC, kinetic thermal processes, depending on time and absolute temperature, often appear in the nonreversing heat flow, while properties with heat effects proportional to the heating rate are found in the reversing heat flow. The latter signal equals the average heating rate times the heat capacity. The specific heat capacity, c_p (J g^{-1} K^{-1}), is calculated as

$$c_p = \frac{A_{\mathrm{HF}}}{A_T \omega} \tag{1}$$

where $A_T\omega$ is the amplitude of the imposed modulated heating rate, with A_T the temperature modulation amplitude (K), ω the modulation angular frequency ($= 2\pi/p$), and p the modulation period (s); A_{HF} is the amplitude (of the first harmonic) of the resulting modulated heat flow (W g^{-1}). The nonreversing heat flow equals the total heat flow (the running average of the modulated signal) minus the reversing heat flow. A

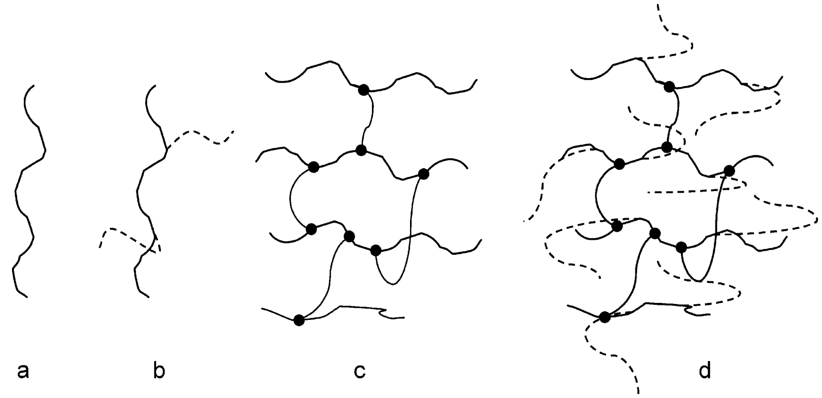
[†] Vrije Universiteit Brussel.

[‡] Ghent University.

* Corresponding author: phone +32-(0)2-629.32.76 or 32.88; FAX +32-(0)2-629.32.78; e-mail bvmele@vub.ac.be.

10.1021/ma035319t CCC: $27.50

Scheme 1. Schematic Representation of the PVCL-Based Systems: (a) Linear PVCL, (b) PVCL-*graft*-PEO, (c) PVCL Network, and (d) PEO-Grafted PVCL Network[a]



[a] PVCL segment (—); PEO segment (- - -); cross-link in PVCL network (●).

complete description of the extraction of the heat capacity and other MTDSC signals can be found in the literature.[12−14]

While the straightforward deconvolution procedure turns out to be valid for the study of reaction rate, chemorheological changes, and structure development in reacting polymer systems,[15−17] it no longer holds for characterizing polymer melting or phase separation in polymer blends and solutions.[2,18−21] Heat effects, coupled with melting/crystallization[18,19] or mixing/demixing,[2,20,21] occur during one modulation cycle and thus contribute to the specific heat capacity calculated by eq 1. Hence, the specific heat capacity is termed “apparent” , c_p^{app}, to distinguish it from the baseline specific heat capacity, c_p^{base}, which is temperature-dependent. The so-called “excess” contribution, c_p^{excess}, is temperature- and time-dependent and changes with the progress of the transformation:

$$c_p^{\mathrm{app}}(T,t) = c_p^{\mathrm{base}}(T) + c_p^{\mathrm{excess}}(T,t) \qquad (2)$$

The ability of MTDSC to study the phase transition behavior in quasi-isothermal conditions (average heating rate equal to zero) by means of the heat capacity signal will be explored in order to obtain information on the kinetics of (re)mixing and demixing of thermo-responsive PVCL-based materials.

Experimental Section

Materials. *N*-Vinylcaprolactam (VCL) (Aldrich, 98%) was recrystallized from benzene and washed several times with hexane before use. 2,2′-Azobis(isobutyronitrile) (AIBN) (Fluka, 99%) was recrystallized from methanol. 2-Propanol was distilled and then refluxed over CaO before use. 1,4-Dioxane and toluene were refluxed over Na/benzophenone until a deep blue color was achieved and subsequently distilled. *N*,*N*′-Methylenebis(acrylamide) (Aldrich, 99+%) was used as received. Triethylamine (Aldrich, 99%) and acryloyl chloride (Acros, 99%) were purified by vacuum distillation before use. Poly(ethylene glycol) methyl ether (PEGME) (Aldrich) was dried by azeotropic distillation in toluene and by further drying under vacuum during 6 h at 80 °C.

Synthesis. *Linear PVCL (Scheme 1a).* VCL (10 wt %) was polymerized in solution, using AIBN (0.05 mol %) as radical initiator.[8] Different solvents were used in order to vary the molar mass of PVCL. The synthesis was performed under nitrogen atmosphere at 70 °C for 12 h. After the reaction, the solution was cooled to room temperature and PVCL was precipitated in diethyl ether (1:10). The polymer was dissolved in a mixture of acetone and water (3:7) and precipitated again by heating the solution to 80 °C. This purification was repeated twice, and then the precipitate was dissolved in water and freeze-dried.

The viscosity-average molar masses (M_v) are 30000 (PVCL 30000), 42000 (PVCL 42000), and 68000 g mol^{-1} (PVCL 68000) from polymerizations in respectively 2-propanol, 1,4-dioxane, and toluene, as was determined from the intrinsic viscosity employing the Mark−Houwink relation $[\eta] = KM^a$ with $K = 0.0105$ mL g^{-1} and $a = 0.69$.[22] The intrinsic viscosity of the PVCL sample was measured with an Ubbelohde-type viscometer at 25 °C using water as solvent.

PVCL-graft-PEO (Scheme 1b). A PVCL-*graft*-PEO copolymer has been synthesized using a grafting onto method. The detailed procedure is described elsewhere and is only briefly summarized.[9]

By the radical copolymerization of VCL and a small amount of *N*-acryloylsuccinimide (NASI), a PVCL backbone with reactive functional groups (PVCL-*co*-NASI; $M_w = 45000$ g mol^{-1}) was prepared. The succinimide groups react easily with a primary amine, such as amino-terminated PEO ($M_w = 5000$ g mol^{-1}). For this study, a PVCL-*graft*-PEO was used consisting of 15.9 wt % PEO, i.e., an average of two PEO grafts per PVCL backbone.

PVCL Network (Scheme 1c). A PVCL network, in the form of a 1 mm thick sheet was obtained as follows: after mixing VCL with methylenebis(acrylamide) (MBAAm, 2 mol %) as a cross-linker at 40 °C for 2 min, 0.5 mol % of AIBN is added. The mixture is degassed for 30 s under vacuum, injected between two hot glass plates (50 °C) separated by a 1 mm silicone spacer and kept at 70 °C for 16 h. The film is removed after 3 h postcuring at 130 °C. The soluble fraction was removed with boiling acetone in a Soxhlet apparatus and is 2%, indicating a high-yield cross-linking reaction.

PEO-Grafted PVCL Network (Scheme 1d). Grafted networks were prepared in a similar way as the PVCL network. Now, acrylate-terminated PEO was added as a comonomer to the reaction mixture in order to introduce PEO grafts onto the PVCL chains. The synthesis of acrylate-terminated PEO as macromonomer starts from the commercially available PEGME ($M_w = 5000$ g mol^{-1}). Into a three-necked flask, equipped with a magnetic stirrer, 0.01 mol of dried PEGME (50 g), 100 mL of CH_2Cl_2, and 0.011 mol of triethylamine (proton trap) were charged under a nitrogen atmosphere. To this mixture, 0.02 mol of acryloyl chloride was added dropwise at a temperature below 10 °C. The esterification reaction proceeded overnight at room temperature. The solution was filtrated several times to remove the precipitated triethylamine hydrochloride salt. The clear liquid was washed with 5% NaOH and several times with distilled water until it became neutral. After treatment with $MgSO_4$ to remove water, the solution was filtered and CH_2Cl_2 was removed by rotary evaporation. Further drying was done under high vacuum at room temperature. A yield of approximately 90% was obtained.

Two PEO-grafted networks were prepared, having an equal (15.9 wt %) and double (31.8 wt %) amount of PEO grafts, compared to PVCL-*graft*-PEO. The soluble fractions are 4 and 10%, respectively. Again, these low values indicate that the cross-linking reaction proceeds with high yields. ^{1}H NMR analysis of the soluble fraction showed a mixture of linear PVCL and unreacted PEO macromonomer in the initial ratio.

Sample Preparation. The polymers were dried under vacuum for a few days at 130 °C, after which the water content was less than 0.5 wt % as determined by thermogravimetric analysis (TA Instruments TGA 2950). The glass transition of dried linear PVCL is 190 °C. Starting from a 10/90 (wt %/wt %) polymer/water solution, a range of compositions were prepared directly in hermetic Perkin-Elmer aluminum pans. Samples containing more than 10 wt % polymer were achieved by evaporation of the water, while those containing less than 10 wt % polymer were attained by dilution of the original 10/90 mixture.

The network/water samples were prepared by adding the appropriate amount of distilled water to dried network directly in Mettler aluminum pans, which are subsequently hermetically sealed.

Each mixture was stored in the refrigerator for at least 48 h to attain a homogeneous sample. A few of these closed crucibles were perforated and the weight loss was measured at 100 °C using TGA to check the preparation procedure (error < 1 wt %).

Modulated Temperature Differential Scanning Calorimetry (MTDSC). The aqueous polymer solutions were measured on a TA Instruments 2920 DSC with the MDSC option and an RCS cooling accessory. Helium was used as a purge gas (25 mL min^{-1}). Indium and cyclohexane were used for temperature calibration. The former was also used for enthalpy calibration. Heat capacity calibration was performed with water, using the heat capacity difference between two temperatures, one above and one below the melting temperature. Standard modulation conditions were an amplitude A_T of 0.5 °C with a period p of 60 s, for both nonisothermal and quasi-isothermal measurements. The nonisothermal experiments were performed at an underlying heating rate of 1 °C min^{-1} unless stated otherwise. Sample weights between 5 and 10 mg were used in Perkin-Elmer hermetic aluminum pans of 30 μL.

The PVCL-based networks were measured in hermetic Mettler aluminum pans on a TA Instruments Q1000 (T-zero technology) with RCS cooling accessory. Nitrogen was used as a purge gas (25 mL min^{-1}). The MTDSC conditions were as stated above.

“Ex-Situ” Gravimetrical Measurements. The swelling degree of the studied networks was determined gravimetrically. After immersion in distilled water at a desired temperature, the samples were removed from the water and tapped with filter paper to remove excess water from the sample surface. The equilibrium weight of the swollen samples was determined after a weight change of less than 1 wt %. The swelling degree was defined as $S = 100(W_{sw} - W_o)/W_o$, where W_{sw} and W_o denote the weight of the swollen and dried sample, respectively.

Results and Discussion

Linear PVCL chains, PVCL-*graft*-PEO copolymers, PVCL networks, and PEO-grafted PVCL networks (Scheme 1) have been prepared to study the differences in demixing behavior of the corresponding PVCL-based aqueous systems.

A. Aqueous Solutions of Linear PVCL and PVCL-*graft*-PEO Copolymers. Nonisothermal Study of PVCL/Water. PVCL/water mixtures show a type I LCST demixing behavior.[8] It represents the “classical” Flory−Huggins miscibility: by increasing the chain length of the polymer, the position of the critical points shifts toward lower polymer concentration. By raising the temperature of a homogeneous solution, phase separation will occur accompanied by an endothermic heat effect.[2,10] Using MTDSC, the demixing enthalpy is completely found in the reversing heat flow signal and as such in the heat capacity. This causes an “apparent” specific heat capacity if calculated by eq 1 with an “excess” contribution due to reversible mixing and demixing on the time scale of the modulation[2] (see introduction and eq 2). The evolution of c_p^{app} for PVCL 42000/water mixtures of two different compositions is shown in Figure 1. Upon heating (Figure 1, thick lines) a deviation is seen from the experimental baseline specific heat capacity, indicating the onset of phase separation. A threshold value of 0.02 J g^{-1} K^{-1}, defined against the extrapolated experimental baseline (Figure 1, dashed lines), was used to determine the demixing temperature of each sample, through which part of the state diagram can be constructed. This approach was already discussed for poly(vinyl methyl ether)/water solutions.[2]

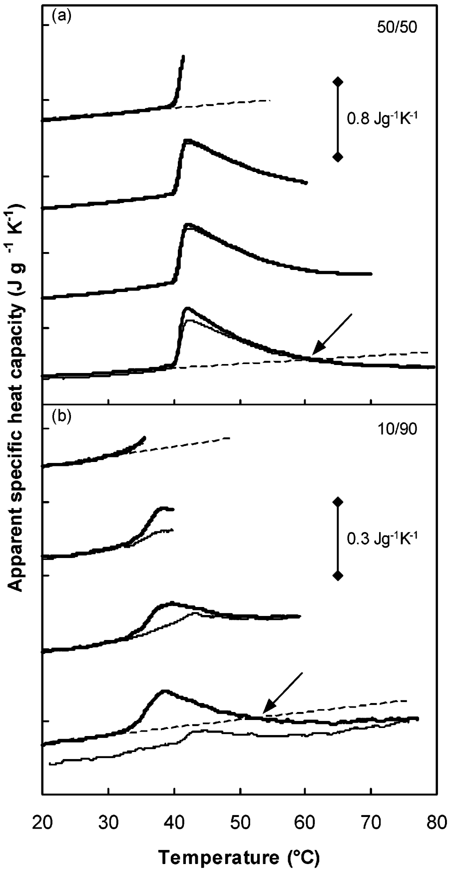


Figure 1. c_p^{app} during nonisothermal demixing (heating: thick) and remixing (cooling: thin) of PVCL 42000/water: (a) 50/50 and (b) 10/90. Curves are shifted vertically for clarity. Dashed line (extrapolated experimental c_p^{base}) is a guide to the eye. Arrow indicates drop of c_p^{app} below c_p^{base} (considered as onset of partial vitrification).

Figure 2a depicts the state diagram of PVCL 42000/water determined by MTDSC. The demixing temperature (Figure 2a, ○) is shown together with the glass transition temperature T_g (Figure 2a, ●) for different compositions. T_g could not be determined for compositions with less than 50 wt % PVCL because the sample could not be cooled sufficiently fast in order to prevent crystallization of water. As expected, T_g lowers with increasing water content due to the plasticizing effect of water on PVCL.[8] The width of the glass transition is also shown (Figure 2a, **I**) because the possible interference of vitrification during phase separation depends

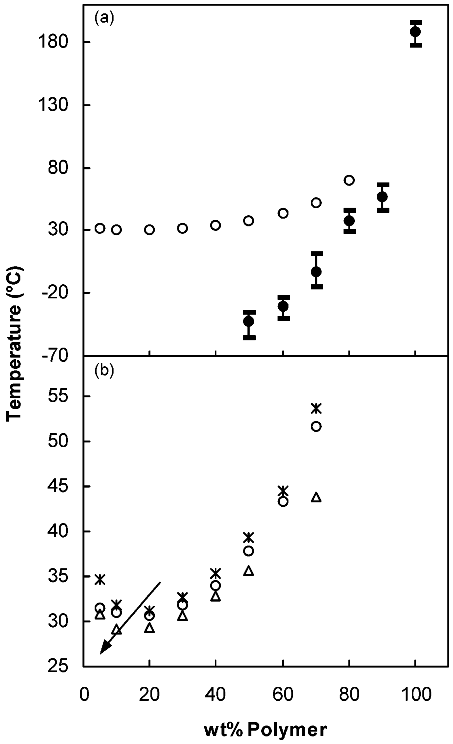


Figure 2. State diagram of (a) PVCL 42000/water, demixing curve (○) and T_g–composition curve (●, width: **I**); (b) demixing curves for PVCL 30000/water (*), PVCL 42000/water (○), and PVCL 68000/water (△). Demixing temperatures are calculated from threshold in c_p^{app} (0.02 J g^{-1} K^{-1}) upon heating and T_g from c_p^{app} upon cooling (5 °C min^{-1}).

on the upper limit of this transition rather than on the average value of T_g.

Figure 2b shows a comparison of the type I LCST demixing behavior of PVCL/water mixtures for different molar masses of PVCL. The critical point shifts to lower temperature and lower polymer concentration for increasing molar mass of the polymer, in agreement with literature.[23]

Influence of Partial Vitrification of PVCL-Rich Phase. A major benefit of using the heat capacity signal from MTDSC is the additional information beyond the demixing temperature.[2] Further heating of PVCL/water solutions induces partial vitrification of the PVCL-rich phase, which is seen as a drop in c_p^{app} below the extrapolated baseline specific heat capacity, indicated by an arrow in Figure 1. This position is influenced by the heating rate (see quasi-isothermal measurements below). The drop in c_p^{app} below c_p^{base} is not the exact onset of partial vitrification due to the effect of c_p^{excess}. The correction is small, however, as the rate of phase separation is decreased by the partial vitrification process; consequently, the contribution of phase separation to c_p^{app} is decreased too, and thus the contribution of c_p^{excess} becomes negligible. At much higher temperatures, near the glass transition of the polymer-rich phase, the specific heat capacity increases toward the extrapolated experimental c_p^{base} (not shown). These structural changes within the sample cannot be deduced from optical microscopy measurements in which the light transmittance drops to zero at the cloud point temperature.

In the subsequent cooling the remixing enthalpy is again found in the reversing heat flow signal and as such in the apparent specific heat capacity. The remixing exotherm is somewhat smaller than the demixing endotherm and hence c_p^{app} (Figure 1a, thin curves), which indicates that the remixing of PVCL/water solutions is slower than the demixing of these systems. However, the missing part of the remixing exotherm is not retrieved in the less sensitive nonreversing heat flow. If the sample was first heated above the onset of partial vitrification (ca. 60 °C), the specific heat capacity value after remixing is smaller than the initial value of the homogeneous solution, indicating a further decrease of the rate of remixing. Upon cooling, water has to diffuse into the vitrified polymer-rich phase, which apparently slows down the remixing kinetics. If the mixture is kept at a temperature in the homogeneous region, c_p^{app} does again increase toward the baseline heat capacity c_p^{base}, as was also seen for partially miscible polymer blends with interference of vitrification.[20,21]

For solutions with less than 20 wt % PVCL (Figure 1b), the observed remixing behavior is totally different. As long as the temperature is kept well below the temperature at which c_p^{app} drops below the extrapolated baseline, the cooling curve for these low PVCL concentrations follows an analogous path as for the other compositions (upper curve of Figure 1b). Starting from higher temperatures, however, the remixing enthalpy is always much lower than the demixing enthalpy, and the specific heat capacity at the end of a cooling curve (after a preceding partial vitrification) is clearly lower than the specific heat capacity of the homogeneous solution at the same temperature (start of a heating curve). Moreover, independent of the molar mass of PVCL, the specific heat capacity remains low and does not regain the initial baseline value, even after long isothermal remixing times. The drop in specific heat capacity at 20 °C is higher using aluminum pans (0.13 J g^{-1} K^{-1}) than using gold-coated high-pressure pans (0.04 J g^{-1} K^{-1}), which might point to different polymer–metal interactions and therefore different adsorption characteristics of the vitrified polymer at the surface of the sample pan. This peculiar behavior is not well understood and needs further investigation.

The magnitude of c_p^{excess} depends on the period of the temperature modulation in relation to the time constant of the phase separation process (inversely proportional to the rate of demixing or remixing). The effect of the period is shown in Figure 3 on both demixing and remixing. c_p^{excess} decreases for smaller periods (higher frequencies). The dynamic range of the MTDSC equipment is not sufficient to level off c_p^{excess} to zero by further increasing the frequency of modulation. Similar results were obtained in a more elaborated study of the effect of the modulation parameters on c_p^{excess} during phase separation of an aqueous poly(vinyl methyl ether) solution.[2]

Influence of PEO Grafting. The PVCL-*graft*-PEO/water solutions were analyzed in a similar way as the PVCL/water samples, leading to the state diagram shown in Figure 4a. Compared to results for linear PVCL with a similar molar mass, the demixing temperatures are lowered due to the introduction of hydrophilic PEO grafts, especially at high polymer concentrations (Figure 4b). For 20 and 70 wt % of polymer, the decrease in demixing temperature is ca. 0.4 and 15.5 °C, respectively. This effect has been investigated in detail earlier.[9,10] A possible explanation is a competition between PVCL and PEO to interact with water, resulting in a weakening of the interactions of PVCL with

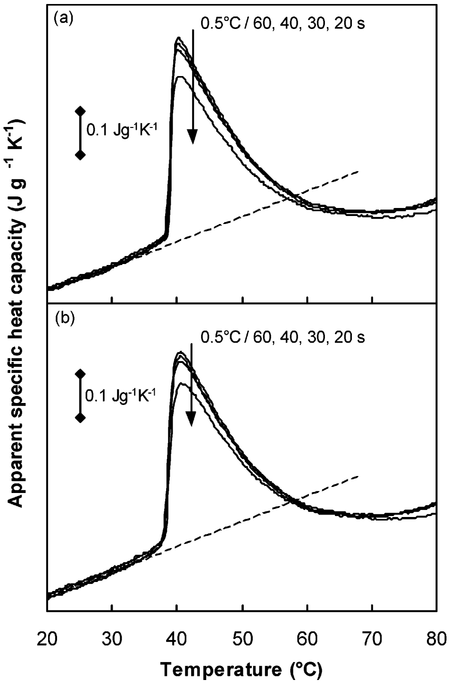


Figure 3. c_p^{app} during nonisothermal demixing (heating, a) and remixing (cooling, b) for 50/50 PVCL 42000/water for different modulation periods: 60, 40, 30, and 20 s.

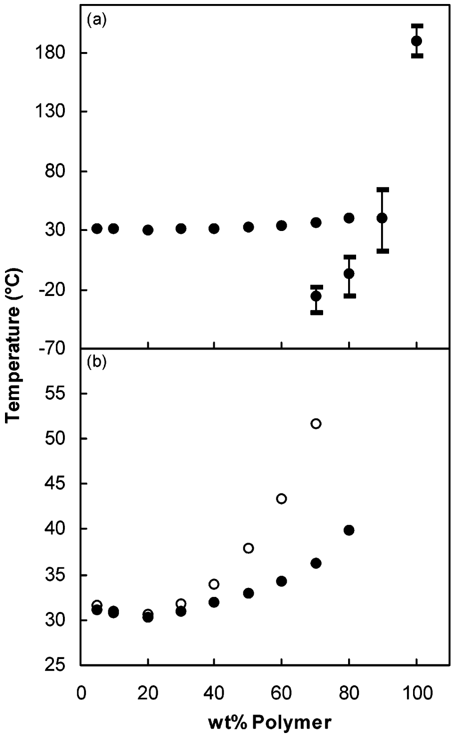


Figure 4. State diagram of (a) PVCL-*graft*-PEO/water, demixing curve (●) and T_g–composition curve (●, width: **I**); (b) demixing curves for PVCL 42000/water (○) and PVCL-*graft*-PEO/water (●). Demixing temperatures are calculated from threshold in c_p^{app} (0.02 J g^{-1} K^{-1}) upon heating and T_g from c_p^{app} upon cooling (5 °C min^{-1}).

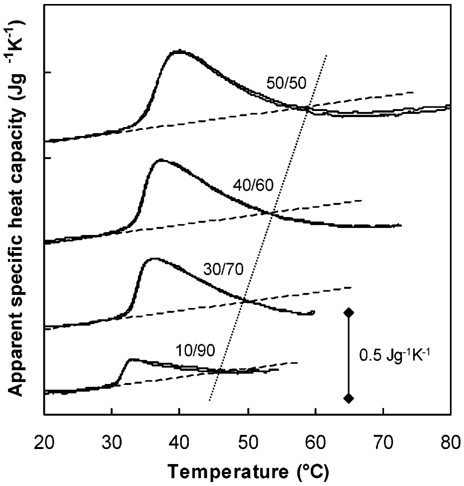


Figure 5. c_p^{app} during nonisothermal demixing (heating) and remixing (cooling) of PVCL-*graft*-PEO/water. Curves for different compositions are shifted vertically for clarity. Dashed line (extrapolated experimental c_p^{base}) is a guide to the eye. Dotted line indicates onset of partial vitrification (heating) or endset of devitrification (cooling).

water in the vicinity of PEO. This will lead to a lowering of the demixing temperature, which becomes more important if less water molecules are available.

The most important difference is that for the PVCL-*graft*-PEO aqueous solutions heating and cooling curves coincide for *each* composition (Figure 5). This indicates that the introduction of PEO grafts influences the kinetics of phase separation and that the rate of remixing is no longer markedly slower than that of demixing, also for the lowest polymer concentration (10/90 PVCL-*graft*-PEO) and even after partial vitrification of the polymer-rich phase. It seems that the PEO grafts are very effective to enhance the rate of phase separation in these systems. Quasi-isothermal MTDSC measurements will be used to further investigate this effect of PEO grafting.

Influence of Polymer Concentration. The onset of partial vitrification during heating or the endset of devitrification during cooling (indicated by a dotted line in Figure 5) is seen at a lower temperature for a lower polymer concentration: compare ca. 60 °C for 50/50 PVCL-*graft*-PEO/water with ca. 45 °C for 10/90 PVCL-*graft*-PEO/water. Note that the same effect is observed for the solutions of linear PVCL (Figure 1). If only the state diagram is taken into account (Figures 2a and 4a), a constant temperature is expected for the onset of vitrification, irrespective of the polymer concentration of the homogeneous solution. The observed trend is also caused by a kinetic effect (see also quasi-isothermal measurements below). The higher the polymer concentration, the smaller the rates of diffusion (and thus the rate of phase separation) and the more the onset of partial vitrification is delayed at a constant heating rate. Similar trends were seen in partially miscible polymer blends.[20,21]

Quasi-Isothermal Study: Kinetics of Partial Demixing and Remixing. By means of quasi-isothermal MTDSC experiments, the time dependency of the apparent specific heat capacity (see eq 2) can be determined. This evolution in time provides information about the kinetics of phase separation of the solutions studied. In Figure 6, quasi-isothermal measurements are compared with a nonisothermal measurement of c_p^{app} for a 50/50 PVCL 42000/water solution. At temperatures below 41.0 °C, no time dependency is noticed, and the quasi-isothermal and the nonisothermal values of c_p^{app} coincide (Figure 6, ○). At temperatures below the demixing temperature (37.9 °C), based on a threshold value of 0.02 J g^{-1} K^{-1} (see discussion above), both quasi-isothermal and nonisothermal values are considered as baseline specific heat capacities. Beyond this

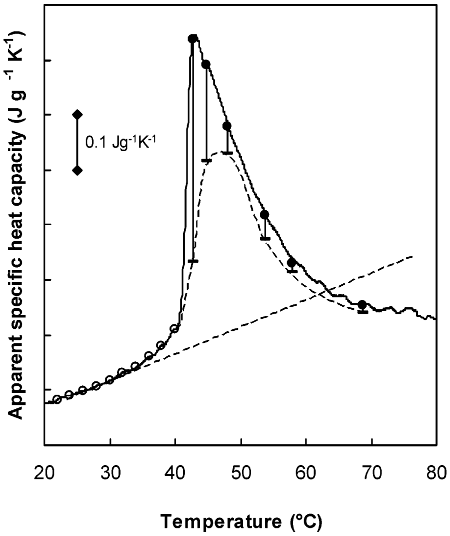


Figure 6. Overlay of the evolution in c_p^{app} for 50/50 PVCL 42000/water: heating curve (demixing); stepwise quasi-isothermal measurements with a step of 2 °C below 41.0 °C (○, equilibrium value); partial quasi-isothermal demixing (42.8, 44.8, 48.0, 53.9, 58.0, and 68.7 °C), starting from a homogeneous mixture at 15.0 °C heated at 1 °C min^{-1} to the respective temperatures: time evolution (vertical lines) from start (●) to end value (—). Dashed lines (extrapolated experimental c_p^{base} and equilibrium c_p^{app}) are a guide to the eye.

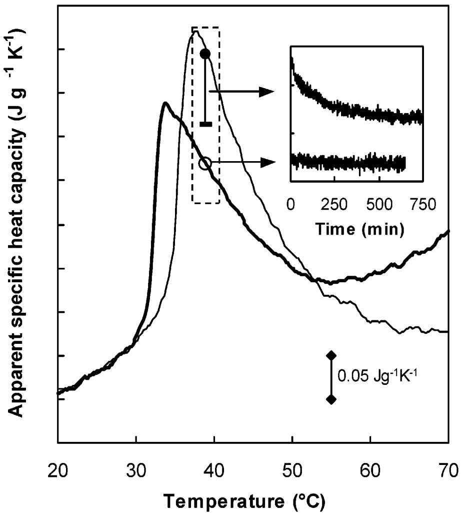


Figure 7. Overlay of the evolution in c_p^{app}: heating curve (demixing) for 20/80 PVCL 42000/water (thin) and 20/80 PVCL-*graft*-PEO/water (thick). Time evolution in c_p^{app} during partial quasi-isothermal demixing at 38.8 °C, starting from a homogeneous mixture at 15.0 °C heated at 1 °C min^{-1} to the quasi-isothermal condition: time evolution (vertical lines) from start (●) to end value (—) for 20/80 PVCL 42000/water (inset: upper curve) and (○, equilibrium value) for 20/80 PVCL-*graft*-PEO/water (inset: lower curve).

temperature a steeper evolution is seen (compare with dashed curve in Figure 6), but the measured specific heat capacity remains time-independent. This deviation cannot be explained on the basis of the temperature dependency of the experimental specific heat capacity of both components. An explanation might be the effect of changing PVCL—water interactions with temperature prior to phase separation. An indication for such an effect can be found in poly(*N*-isopropylacrylamide) hydrogels, where fluorescence labeling shows a decrease in the maximum wavelength before T_{CP}.[24] Dynamic light scattering (DLS) measurements also suggest a change in coil dimensions of a fraction of PVCL chains prior to phase separation.[25] The changing PVCL—water interactions with temperature might cause an extra contribution to the specific heat capacity of the homogeneous solution, so that a straightforward additivity of the experimental specific heat capacities of the pure components is no longer valid. Still, this deviation from c_p^{base} should be related to a fast process within the sample, since equilibrium is immediately reached.

At temperatures above 41.0 °C, c_p^{app} is clearly time-dependent until an equilibrium excess contribution is attained, as indicated by vertical lines in Figure 6 (start (●), end value (—)). This slow evolution, which takes about 1 day, is due to morphological changes or interphase development within the sample. Note that the value of c_p^{app} at equilibrium is up to 15% or ca. 0.3 J g^{-1} K^{-1} higher than the tentative experimental baseline specific heat capacity, indicating the importance of the remaining excess contribution. The dashed curve connecting the measured values of c_p^{app} at equilibrium is shown in Figure 6. From this curve it is clear that the drop in c_p^{app} below c_p^{base} is detected ca. 2 °C sooner than in the case of heating at 1 °C min^{-1}. This influence of heating rate is caused by the kinetics of phase separation and the effect of the partial vitrification process on the kinetics. The effect of heating rate (and quasi-isothermal measurements) on the position of the drop in c_p^{app} below c_p^{base} is also observed and is much more pronounced in the case of partially miscible polymer blends.[21]

The cloud point temperature T_{CP} determined by optical microscopy in a hot stage (41.5 °C) is higher (ca. 3.6 °C) than the demixing temperature based on c_p^{app} and a threshold value of 0.02 J g^{-1} K^{-1}. This difference could mean that MTDSC is able to detect the initiation of smaller particles (in comparison to optical microscopy with the highest sensitivity at ca. 615 nm).

When comparing 20/80 PVCL/water (Figure 7, thin curve) with 20/80 PVCL-*graft*-PEO/water solutions (Figure 7, thick curve), one can clearly see that the slow time evolution for the linear polymer (Figure 7, inset: upper curve) is no longer present for the grafted polymer (Figure 7, inset: lower curve). For the PVCL-*graft*-PEO systems, the equilibrium excess contribution is immediately attained at each temperature within the demixing region (for example 38.8 °C), irrespective of the sample composition. This observation is valid for demixing and remixing experiments. The fact that PEO grafts are very effective to enhance the rate of phase separation, and especially the rate of remixing is further illustrated in Figure 8. The quasi-isothermal remixing at 10 °C of 50/50 PVCL 42000/water and 50/50 PVCL-*graft*-PEO/water is compared after a preceding heating to 90 °C (demixing with partial vitrification). It is obvious that the grafted system already remixed during cooling from 90 to 10 °C, so that the measured specific heat capacity at 10 °C is time-independent and equal to the expected value for c_p^{base}. On the contrary, the nongrafted system is remixing much slower and has to devitrify further (for at least 2 h) before reaching again the initial level of c_p^{base} for the homogeneous mixture at 10 °C (indicated by a dashed line in Figure 8). After complete remixing, however, a second demixing in a subsequent heating is identical to the first one, indicating the reversibility of the process. These quasi-isothermal MTDSC results are in agreement with the idea that the PEO grafts act as mobile water channels,

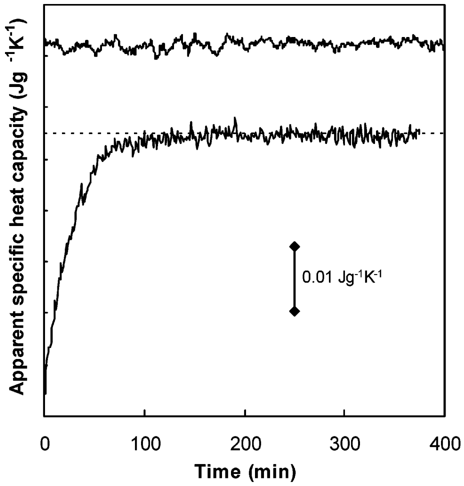


Figure 8. c_p^{app} during quasi-isothermal remixing at 10 °C for 50/50 PVCL 42000/water and 50/50 PVCL-*graft*-PEO/water after heating (demixing) up to 90 °C. Curves are shifted vertically for clarity. c_p^{base} at 10 °C is indicated (dashed line).

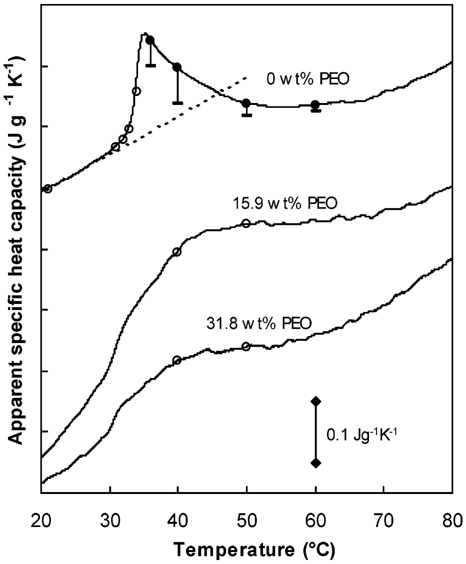


Figure 9. Overlay of the evolution in c_p^{app} for 25/75 PVCL network/water with varying amounts of PEO (0, 15.9, and 31.8 wt %): heating curves (demixing); partial quasi-isothermal demixing at 20.0, 31.0 to 34.0, 36.0, 40.0, 50.0, and 60.0 °C (0 wt % PEO), at 40.0 and 50.0 °C (15.9 and 31.8 wt % PEO), starting from a homogeneous mixture at 15.0 °C heated at 1 °C min^{-1} to the respective temperature: time evolution (vertical lines) from start (●) to end value (—) or (○, equilibrium value if no time dependency). Curves for different compositions are shifted vertically for clarity. Dashed line (extrapolated experimental c_p^{base}) is a guide to the eye.

which enhance the rate of water exchange and thus the rate of demixing/remixing.[7] These findings will further be explored for PVCL-networks.

B. Hydrogels of PVCL Networks and PEO-Grafted PVCL Networks. Kinetics of Partial Demixing and Remixing. Network systems have more practical applications than the related aqueous solutions (see introduction).[1,4,5] Therefore, the incorporation of PEO grafts within the PVCL network and the effect on the kinetics of phase separation are studied for different wt % of PEO grafts. Figure 9 shows the phase behavior of PVCL network/water (25/75) with 0, 15.9, and 31.8 wt % of PEO grafts. The high water content ensures that the networks are swollen to equilibrium in the homogeneous region; i.e., the addition of more water does not lead to further swelling of the networks. Upon heating, the PVCL networks will shrink, and as for the aqueous PVCL solutions, this is seen as a deviation from the baseline specific heat capacity (Figure 9, dashed line). As for the linear PVCL system, the demixing temperature of the pure PVCL network (32.7 °C) is lowered by the introduction of PEO grafts: 2.9 and 4.1 °C for the PVCL network with 15.9 and 31.8 wt % PEO grafts, respectively.

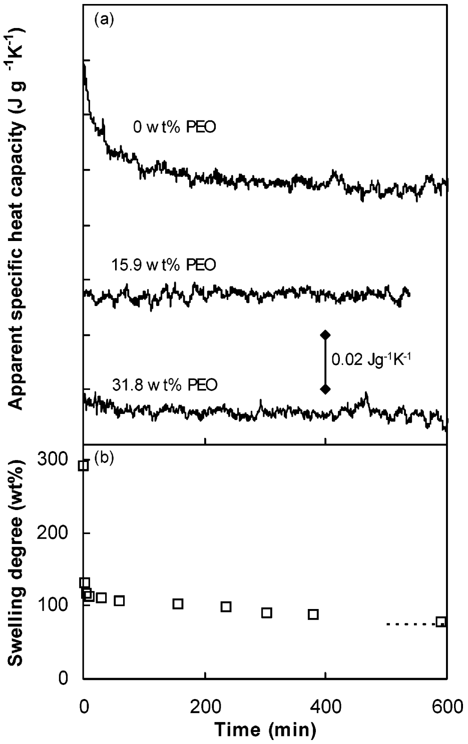


Figure 10. Quasi-isothermal demixing at 40.0 °C for 25/75 PVCL network/water: (a) time evolution of c_p^{app} for varying amounts of PEO (0, 15.9, and 31.8 wt %). c_p^{app} curves for different compositions are shifted vertically for clarity; (b) comparison with swelling degree from gravimetric analysis (0 wt % PEO), time evolution (□), and swelling degree after 1390 min (- - -).

The most striking effect of the PEO grafts is again noticed on the rate of (de)swelling. For the PVCL network without grafts the remixing (swelling) is slower than the demixing (shrinking), while for the networks with PEO grafting the heating and cooling curves coincide, irrespective of the water content. An analogous behavior was noticed for the linear PVCL systems.

Quasi-isothermal experiments at different temperatures were performed for each network to study this kinetic effect in more detail. For the PVCL network without PEO grafts, no time dependency is noticed below the demixing temperature of 32.7 °C (Figure 9, ○). Just above this temperature a deviation is seen from the extrapolated baseline, but the measured specific heat capacity remains time-independent. This deviation might again be caused by changing PVCL−water interactions prior to network shrinkage (related to fast processes on the time scale of the modulation). Mikheeva et al. described this phenomenon as a microsegregation in the gel, prior to the actual volume collapse.[26]

In the demixing region (above 34.1 °C), a slow time evolution to an equilibrium state is again observed (Figure 9, vertical lines; Figure 10a, upper curve). Figure 10a shows an evolution for several hours in c_p^{app}

at 40 °C for the pure PVCL hydrogel. For the networks with PEO grafts (15.9 and 31.8 wt %), the rate of demixing is enhanced because no time dependency is seen, even at temperatures within the phase separation region, which is illustrated at 40 °C (Figure 10a) and also at 50 °C (Figure 9, ○).

As shown in Figure 10b, the time dependency over a long time interval for the pure PVCL hydrogel (0 wt % PEO) is also found by "ex-situ" gravimetrical measurements. In this analysis, the macroscopic shrinkage (or swelling degree) is determined by the amount (weight) of water retained in the network. The equilibrium swelling degree is not attained after 600 min (□), and macroscopic shrinkage continues at least up to 1390 min (- - -). The discontinuous gravimetrical technique does not allow to characterize the faster shrinking of a PEO-grafted network in a reproducible and quantitative way. The similar trend for the pure PVCL hydrogel observed with the discontinuous "ex-situ" gravimetrical measurements and the continuous "in situ" monitoring by heat capacity measurements with MTDSC is interesting. While both gravimetry and MTDSC give macroscopic information on the sample, the latter technique might provide additional information on the molecular level. Indeed, the time-dependent macroscopic shrinking of the networks is caused by nanoscale processes in the polymer/water interphase like hydration/dehydration of the polymer segments. The latter phenomena can be monitored with MTDSC in quasi-isothermal conditions by means of c_p^{excess} (eq 2).[2] The observed time dependency over a long time interval can be associated with a slow decrease of the interphase fraction in the hydrogel toward an equilibrium.

Conclusions

Modulated temperature DSC has been used to study the LCST behavior and the phase separation kinetics of linear PVCL, PVCL-*graft*-PEO, PVCL networks, and PEO-grafted PVCL networks. The type I LCST-phase behavior of aqueous PVCL-based systems has been confirmed. The onset of phase separation is determined by the specific heat capacity signal upon heating.

For linear PVCL/water solutions the smaller reversing heat flow contribution found upon cooling indicates that remixing is slower than demixing. This effect is emphasized by a partial vitrification of the PVCL-rich phase. A higher polymer concentration is also slowing down the rate of phase separation. On the other hand, it has been demonstrated that the introduction of PEO grafts enhances the remixing kinetics, which is expressed in similar heating and cooling curves of the apparent specific heat capacity. PEO grafts have an analogous effect on PVCL network/water systems and increase the (de)swelling rate of these hydrogels.

MTDSC also enables to study quasi-isothermally the slow processes occurring in the PVCL/water solution. The slow morphology development can take up to 1 day before equilibrium is achieved. The observed time dependency over a long time interval can be associated with the specific interactions of water molecules surrounding the polymer chains. The fraction of this important polymer/water interphase probably slowly decreases toward an equilibrium condition (nanoscale information). This equilibrium condition at any temperature in the phase separation region is immediately attained by the introduction of PEO grafts. As such, the increase of the (de)swelling rate of thermoresponsive hydrogels by the introduction of hydrophilic chains such as PEO can be explained by the higher diffusion rate of water molecules in the interphase surrounding these mobile chain segments.

Acknowledgment. Kurt Van Durme and Sam Verbrugghe thank the Flemish Institute for the Promotion of Innovation through Science and Technology in Flanders (I.W.T.) for a Ph.D. grant. The Supernet programme of the European Science Foundation (E.S.F.) is acknowledged for financial support.

References and Notes

(1) Hoffman, A. S. *Macromol. Symp.* **1995**, *98*, 645−664.
(2) Swier, S.; Van Durme, K.; Van Mele, B. *J. Polym. Sci., Polym Phys* **2003**, *41*, 1824−1836.
(3) Christova, D.; Velichkova, R.; Loos, W.; Goethals, E. J.; Du Prez, F. E. *Polymer* **2003**, *44*, 2255−2261.
(4) Markvicheva, N. A.; Tkachuk, N. E.; Kuptsova, S. V.; Dugina, T. N.; Strukova, S. M.; Kirsh, Y. E.; Zubov, V. P.; Rumsh, L. D. *Appl. Biochem. Biotechnol.* **1996**, *61*, 75−84.
(5) Kirsh, Y. E. In *Water-Soluble Poly-N-vinylamides*; J. Wiley & Sons: Chichester, 1998; Chapter 3, p 81.
(6) Yan, Q.; Hoffman, A. S. *Polymer* **1995**, *36*, 887−889.
(7) Kaneko, Y.; Nakamura, S.; Sakai, K.; Aoyagi, T.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Macromolecules* **1998**, *31*, 6099−6105.
(8) Meeussen, F.; Nies, E.; Verbrugghe, S.; Goethals, E.; Du Prez, F.; Berghmans, H. *Polymer* **2000**, *41*, 8597−8602.
(9) Verbrugghe, S.; Bernaerts, K.; Du Prez, F. E. *Macromol. Chem. Phys.* **2003**, *204*, 1217−1225.
(10) Yanul, N. A.; Kirsh, Y. E.; Verbrugghe, S.; Goethals, E.; Du Prez, F. *Macromol. Chem. Phys.* **2001**, *202*, 1700−1709.
(11) Verbrugghe, S.; Laukkanen, A.; Aseyev, V.; Tenhu, H.; Winnik, F. M.; Du Prez, F. E. *Polymer* **2003**, *44*, 6807−6814.
(12) Reading, M.; Luget, A.; Wilson, R. *Thermochim. Acta* **1994**, *238*, 295−307.
(13) Wunderlich, B.; Jin, Y.; Boller, A. *Thermochim. Acta* **1994**, *238*, 277−293.
(14) Reading, M. *Trends Polym. Sci.* **1993**, *8*, 248−253.
(15) Van Assche, G.; Van Hemelrijck, A.; Rahier, H.; Van Mele, B. *Thermochim. Acta* **1995**, *268*, 121−142.
(16) Swier, S.; Van Mele, B. *J. Polym. Sci., Polym. Phys.* **2003**, *41*, 594−608.
(17) Swier, S.; Van Mele, B. *Macromolecules* **2003**, *36*, 4424−4435.
(18) Ishikiriyama, K.; Wunderlich, B. *J. Polym. Sci., Polym. Phys.* **1997**, *35*, 1877−1886.
(19) Minakov, A. A.; Schick, C. *Thermochim. Acta* **1999**, *330*, 109−119.
(20) Dreezen, G.; Groeninckx, G.; Swier, S.; Van Mele, B. *Polymer* **2001**, *42*, 1449−1459.
(21) Swier, S.; Pieters, R.; Van Mele, B. *Polymer* **2002**, *43*, 3611−3620.
(22) Kirsh, Y. E.; Yanul, N. A.; Kalninsh, K. K. *Eur. Polym. J.* **1999**, *35*, 305−316.
(23) Šolc, K.; Dušek, K.; Koningsveld, R.; Berghmans, H. *Collect. Czech. Chem. Commun.* **1995**, *60*, 1661−1688.
(24) Iwai, K.; Hanasaki, K.; Yamamoto, M. *J. Lumin.* **2000**, *87−89*, 1289−1291.
(25) Makhaeva, E. E.; Tenhu, H.; Khokhlov, A. R. *Polymer* **2000**, *41*, 9139−9145.
(26) Mikheeva, L. M.; Grinberg, N. V.; Mashkevich, A. Y.; Grinberg, V. Y.; Thanh, L. T. M.; Makhaeva, E. E.; Khokhlov, A. R. *Macromolecules* **1997**, *30*, 2693−2699.

MA035319T