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Ordering and structure formation in triblock copolymer solutions.
Part II. Small angle X-ray scattering and calorimetric observations

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The morphology and thermal properties of a poly(styrene)–poly(ethylene, butylene) triblock copolymer in the presence of a selective solvent has been investigated, using small-angle X-ray scattering (SAXS) and calorimetry (d.s.c.). The temperature dependence of the SAXS profiles indicated a transition, which was associated with a thermal destruction of the superlattice, preserving the nearest neighbour distance between the micro domains. The transition temperature was referred to as the disordering temperature (T_d). On heating, the loss of long range order was observed as a sudden broadening of the line profiles of the first order peak. At higher temperatures a gradual disappearance of this first order peak was interpreted as a gradual dissolution of the micro domain structure. Simultaneously, calorimetric investigations revealed two transitions on heating: at lower temperatures a glass transition, followed by an endothermic transition. The onset of the endotherm corresponded to T_d. In addition, the onset of flow, which has been reported in Part I of this series, also corresponded to T_d. Annealing at intermediate temperatures resulted in the formation of large scale ordering. This ordering could be followed by X-ray scattering and corresponded to changes observed in the rheological behaviour. © 1997 Elsevier Science Ltd.

(Keywords: block copolymer; disordering temperature; micro phase separation)

INTRODUCTION

In a previous paper of this series[1], we presented the temperature dependence of the rheological properties of poly(styrene)–poly(ethylene, butylene)–poly(styrene) triblock copolymers, in the presence of a selective solvent. However, in order to define the different transitions observed, detailed morphological and calorimetric information are needed.

The properties of block copolymers in the presence of solvents have been extensively studied in literature[4–12]. In the higher concentration region, concentrations above 5%, different research groups showed experimentally that the microphase separation temperature decreases on adding a solvent that is selective for one of the segments. In addition, Hashimoto *et al.*, Shibayama *et al.* and Watanabe *et al.* investigated the influence of solvent on the micro domain structure and on the superlattice by rheological and scattering techniques. Their results revealed the occurrence of two thermal transitions on heating: (a) at lower temperatures a transition is observed, associated with a thermal destruction of the superlattice of the micro domains. This transition is referred to as the lattice disordering and is observed in SAXS as a sudden increase of the line profiles of the first order peak and an overlap or extinction of higher order peaks. (b) At higher temperatures a transition occurs that invokes a dissolution of the micro domain structure, and corresponds to a disappearance of the first order scattering maximum itself.

EXPERIMENTAL

Materials and sample preparation

The characteristics of the polymer sample and the extender oil are described in part I of this series. The samples used for the X-ray measurements were identical to the samples used in the rheological experiments. In order to prepare samples for calorimetry, the polymer and the extender oil were sealed in a glass tube. Homogenization was obtained by rotating the glass tubes in hot silicone oil. Afterwards the cooled samples were transferred into d.s.c.-pans.

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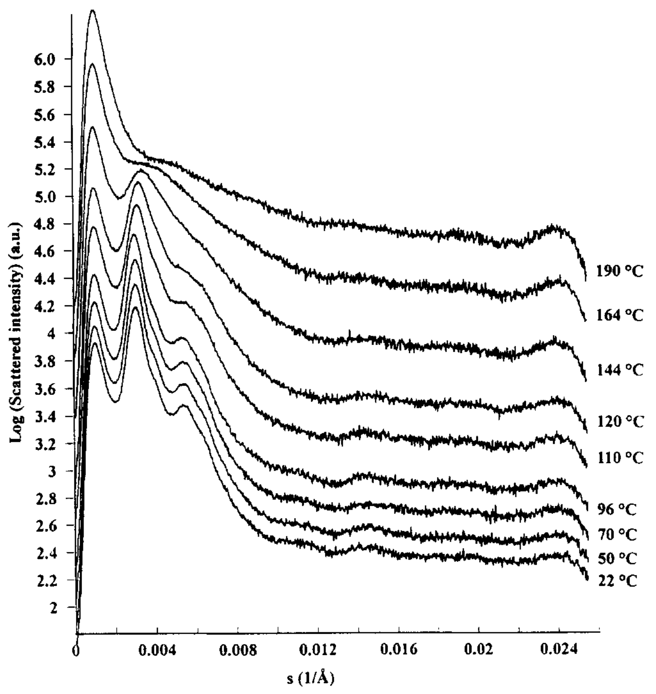

Figure 1 SAXS curves recorded on heating a SEBS-20% sample. The heating rate was $2\,\mathrm{K\,min^{-1}}$. The exposure time was 30 s

Calorimetry

The thermal behaviour was studied by d.s.c. (DSC7, Perkin–Elmer). Large volume pans containing 40 mg were used. Measurements were performed between 25°C to 250°C at a scanning rate of $10\,\mathrm{K\,min^{-1}}$.

SAXS equipment

The isothermal SAXS measurements were carried out with Ni-filtered Cu*Kα* radiation on a Kratky-type camera (Rigaku) with a 40 μm entrance slit installed on a Rigaku Rotaflex rotating anode, operated at 4 kW. The data were obtained with infinite slit geometry using a linear position-sensitive proportional detector (Braun OED-50M) to measure the scattered intensity. These data were desmeared and corrected for background scattering using the FFSAXS5 program by Vonk, as reported in ref. 2.

The dynamic or time-resolved SAXS measurements are performed with a point focus and the X33 camera[13,14] of the European Molecular Biology Laboratory (EMBL) in HASYLAB on the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY) at Hamburg. Temperature control is accomplished with a Mettler FP90 hot stage. The SAXS profiles are recorded during 30 s. The heating rate is $+2°\mathrm{C\,min^{-1}}$ and a rate of $5°\mathrm{C\,min^{-1}}$ is chosen for cooling.

RESULTS

SAXS measurements

Dynamic measurements. The morphology of these triblock copolymer gels at room temperature has been reported previously[2,3]. The scattering curves exhibit two maxima in the low angle region, a strong one and a weaker one, followed by a steep decrease in intensity, and a broad maxima in the tail of the small angle region. The two low-angle peaks were attributed to an interdomain interference, and the maximum at higher angle was attributed to the form factor of the phase separated PS-domains. All the investigated samples had a microphase separated structure at room temperature and a hexagonal arrangement of the polystyrene domains was assumed.

In order to correlate rheological and morphological properties, SAXS patterns were recorded at higher temperatures. In *Figure 1* experimentally measured curves of an as-prepared sample, SEBS-20%, are presented. The sample was heated at $2°\mathrm{C\,min^{-1}}$. The recording time for one SAXS curve was 30 s. Up to 105°C, the diffraction pattern does not change and the scattering curves are superimposable. The change induced in the sample by crossing the glass transition temperature, as will be discussed later, apparently does not affect the scattering curves. But once the temperature exceeds 105°C, the main diffraction maximum shifts to larger angles, the width increases and the intensity decreases. This indicates clearly that a transition takes place around this temperature. A further increase in temperature results in a continuous decrease of the scattered intensity, a further broadening of the primary peak, a shift of the maximum of this signal and the disappearance of the second order maximum. Therefore, it seems to us that only one transition takes place, namely the one at 105°C and that the sample then evolves gradually towards a homogeneous solution at very high temperature. This is confirmed by a plot of the reciprocal intensity of this primary peak and its position as a function of the reciprocal temperature, *Figure 2*. A transition clearly takes place at 105°C. But a linear extrapolation of the reciprocal intensity vs. the reciprocal temperature is not possible in the high temperature region. This relationship shows a continuous curvature, and is in contradiction with the theoretical prediction made for solvent free block copolymers and recently reported experimental data[11,15–22].

The transition at 105°C is also responsible for the onset of flow, discussed in Part I, and is associated with a d.s.c. signal. The transition temperature will be called the disordering temperature (T_d) in order to avoid any possible conflict with other definitions presented in literature.

Isothermal annealing. The rheological properties indicated a gel formation during isothermal annealing at higher temperatures, therefore, the influence of time on the SAXS pattern of an SEBS-20% sample is also investigated. The evolution of the SAXS pattern during isothermal annealing at 100°C is presented in *Figure 3*. In these experiments the exposure time for one SAXS scan was 30 min. The SAXS curve, measured within the first 30 min after the sample reached 100°C, is nearly similar to the SAXS pattern recorded at room temperature. But after annealing between 30 and 60 min at 100°C, additional peaks appear and an overall sharpening of the diffraction signals is observed. Comparing this with the mechanical properties, annealing at 100°C, induced a gel formation in the sample. A detailed analysis of the changes observed in the SAXS pattern, during annealing, will be presented later[23].

Annealing also increases the stability of the structure as no changes are observed if the sample is brought to 110°C. AT 120°C however, the additional peaks disappear and the pattern becomes similar to the one recorded with the as-prepared samples. This corresponds

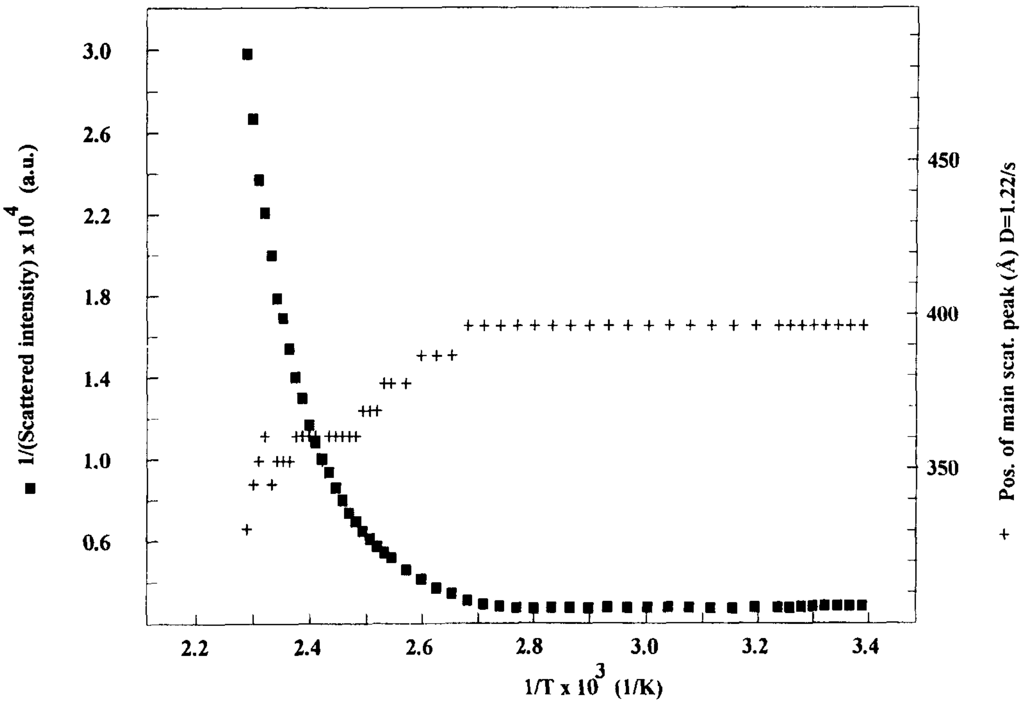

Figure 2 Reciprocal intensity plot for SEBS-20%, deduced from *Figure 1*

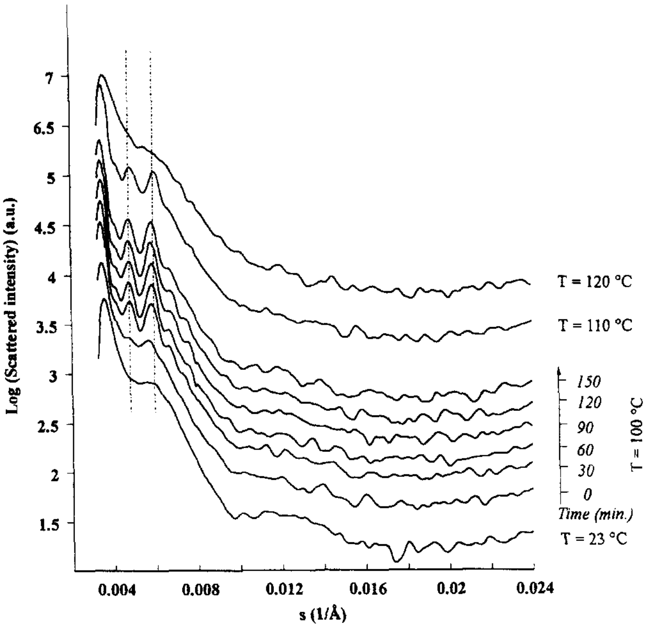

Figure 3 Scattering curves measured during isothermal annealing at 100°C for SEBS-20%. Temperatures and times are indicated. (The time corresponds to the time at which the SAXS measurement was started.) Exposure time is 30 min

again with the rheological observations; after annealing the flow temperature of the sample increased from 105°C to 118°C. Further treatment at 120°C does not induce any changes in the structure nor in the rheological properties.

The additional diffraction peaks and the increased sharpness are maintained when an annealed sample is cooled to room temperature.

Calorimetry

SEBS-20% sample. A sample with 20% polymer was left at room temperature for some days, after it was prepared at 200°C. Then it was transferred to the d.s.c.-pan and heated in the d.s.c. Two transitions can be observed. Around 60°C, a transition characteristic for the occurrence of a glass transition takes place. This transition is followed at higher temperature, between 100°C and 135°C, by a well-defined peak. In d.s.c., transitions are only observed during the first heating scan, recorded some days after preparation of the samples. If the sample however, is left at room temperature for a longer period of time of the order of 1 week, the transitions can again be observed. The shape of the calorimetric signal and its position on the temperature scale can be very well reproduced. A typical example is given in *Figure 4*.

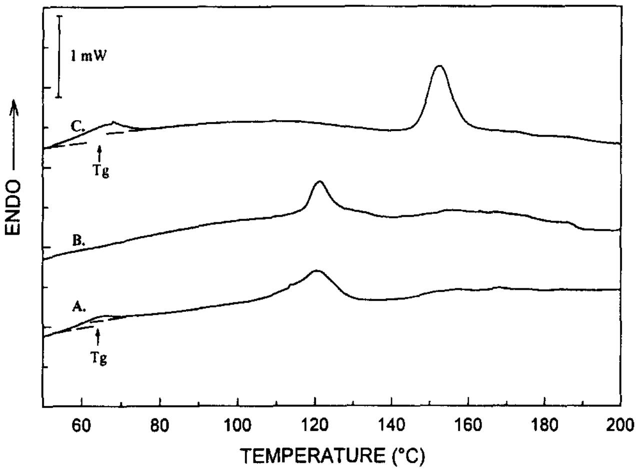

Figure 4 D.s.c.-heating scans. (A) SEBS-20%, after annealing at room temperature. (B) SEBS-20%, after annealing at 100°C. (C) SEBS-30%, after annealing at room temperature (rate = 10 K min^{-1})

D.s.c. measurements were also performed after annealing at 90°C and 100°C. Again an endothermic transition is observed, the thermogram is also presented in *Figure 4*. On comparing the two d.s.c. curves, the one

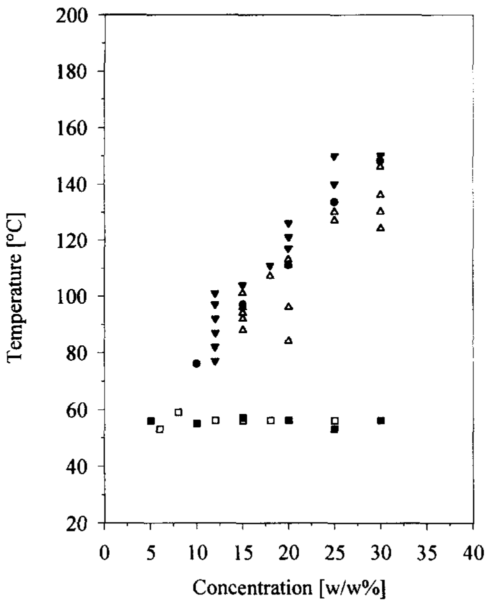

Figure 5 Temperature–concentration diagram for SEBS-extender oil. The d.s.c. measurements were recorded after annealing at room temperature (glass transition ■, onset of endotherm ●), the rheological data were recorded after annealing at higher temperatures (glass transition □, time influence △, no time influence ▼)

measured after annealing at room temperature and the one measured after annealing at 100°C, we see that for the sample annealed at 100°C, the onset temperature of the endotherm is shifted to higher temperatures and the endotherm is sharper. The temperature at the onset of this endotherm corresponds to the temperature at which an annealed gel, in the course of a rheological measurement, starts flowing, and with the temperature, at which the additional peaks in the SAXS curves after annealing, disappear again.

Influence of polymer concentration. The influence of extender concentration on the thermal transitions was investigated. In *Figure 4* a d.s.c.-heating scan of a SEBS-30% sample, annealed at room temperature, is also presented. It is seen that the transitions are concentration dependent. In *Figure 5* the onset temperatures of the calorimetric signals, recorded after annealing at room temperature, are plotted as a function of concentration. If we compare these measurements with the rheological data we see that the concentration dependence of the endothermic transition corresponds to the rheologically determined temperatures, also shown in *Figure 5*. In diluted samples, concentrations below 15%, the endothermic transition was weak but still present. In *Figure 5*, glass transition temperatures detected with d.s.c. and rheology are also indicated. A nice correlation between the two techniques is found.

DISCUSSION

Glass transition of the polystyrene phase

The glass transition observed in d.s.c. experiments corresponds very well with the softening in rheology. The d.s.c. signal however can only be observed after annealing at room temperature. This annealing at room temperature close to the glass transition results in an enthalpy relaxation at T_g that manifests itself as an endothermic signal. Only the presence of this signal makes it possible to localize the transition. Without annealing only a shift in the baseline should be observed. But at the low polystyrene concentration used in these experiments, such a shift cannot be distinguished from the baseline noise. In the SAXS experiments no pronounced changes were observed at these low temperatures. This transition coincides on the temperature scale with the one represented in Part I[24].

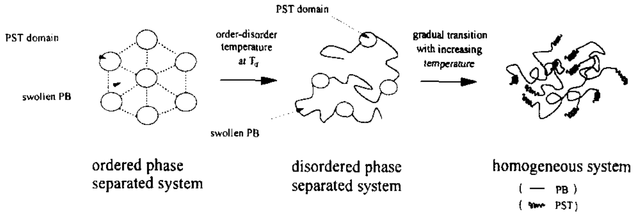

Figure 6 Schematical evolution of the structure of a non-annealed sample on heating

Disordering temperature, T_d

The combination of data obtained from rheological observations, calorimetric measurements and SAXS-scattering measurements leads to the conclusion that only one transition takes place in the higher temperature region. In a non-annealed SEBS-20% sample, this transition sets in at 105°C. Annealing can shift this transition to higher temperatures while improving the lattice structure. For an SEBS-20% sample, annealing can shift the transition temperature to 118–120°C. On further heating above this limiting temperature, a continuous change towards an isotropic solution takes place. The transition is fully reversible and the gel is also formed on cooling. The disordering temperature can be localized by different experimental methods used in this study. The evolution of a non-annealed sample during heating is schematically shown in *Figure 6*.

(a) At T_d, the gels transform from a rather elastic material into a liquid-like, flowing system. This transition cannot be related to the isotropization temperature, generally discussed in literature and referred to as T_{ODT} or T_{MST}.

(b) The thermograms obtained by d.s.c. observations are characteristic for an order–disorder transition. This observation however, can only be made with annealed samples and not with samples recorded immediately after cooling to room temperature. Annealing has to be performed at high temperature for a period of hours, or at room temperature for several days. This can be ascribed to the need to develop long range order over larger scales, before a calorimetric signal can be observed. This can only be realized by long-time annealing.

(c) Two important conclusions can be drawn from the SAXS observations. The transformation of the hexagonal symmetry into another arrangement can be the result of a change of the volume fraction of the PS domains. Extender oil can penetrate these domains and therefore change their size. This will result in a different three-dimensional packing, which is maintained when the sample is cooled to room temperature.

The evolution from a phase separated, organized system towards an isotropic solution at very high temperature takes place in two steps. At T_d, the long range order disappears. A further increase in temperature will lead to a homogeneous system by a mutual interpenetration of the different constituents. This will manifest itself in a further change in size, composition and therefore in the density of the domains and will change the overall shape of the SAXS curve and their position on the scattering vector scale.

CONCLUSIONS

The following important conclusions can be drawn.

(1) The phase separated, triblock copolymer gels show two thermal transitions: a glass transition of the polystyrene domains at T_g and a disordering transition at T_d. The temperature at which this last transition takes place depends on the thermal history of the sample. Its formation is fully reversible and the influence of polymer concentration and annealing temperature is well established.

(2) The position of T_g on the temperature scale suggests the presence of small quantities of oil ($<2\%$) in the polystyrene domains. This transition can be observed by rheology and calorimetry but does not affect the SAXS observations.

(3) Annealing stabilizes the phase separated structure and increases the degree of order. The formation of another lattice symmetry is observed. This transition is observed in the thermal, mechanical and morphological properties of the sample. This additional structure is maintained after cooling to room temperature.

(4) Further heating above T_d will bring the sample from the phase separated, disordered state, towards the homogeneous state. The different experimental observations however, do not allow for an exact determination of this isotropization temperature which is estimated to be close to 200°C.

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REFERENCES

1. Soenen, H., Berghmans, H., Winter, H. H. and Overbergh, N., *Polymer*, 1997, **38**, 5653.
2. Mischenko, N., Reynders, K., Mortensen, K., Scherrenberg, R., Fontaine, F., Graulus, R. and Reynaers, H., *Macromolecules*, 1994, **27**, 2345.
3. Mischenko, N., Reynders, K., Koch, M. H. J., Mortensen, K., Pedersen, J. S., Fontaine, F., Graulus, R. and Reynaers, H., *Macromolecules*, 1995, **28**, 2054.
4. Watanabe, H., Kotaka, T., Hashimoto, T., Shibayama, M. and Kawai, H., *J. Rheol.*, 1982, **26**(2), 153.
5. Watanabe, H., Kuwahara, S. and Kotada, T., *J. Rheol.*, 1984, **28**(4), 393.
6. Kraus, G. and Hashimoto, T., *J. Appl. Polym. Sci.*, 1982, **27**, 1745.
7. Kim, J., Han, C. D. and Chu, S. G., *J. Polymer Sci., Polym. Phys. Ed.*, 1988, **26**, 677.
8. Shibayama, M., Hashimoto, T. and Kawai, H., *Macromolecules*, 1983, **16**, 16.
9. Hashimoto, T., Shibayama, M., Kawai, H., Watanabe, H. and Kotaka, T., *Macromolecules*, 1983, **16**, 361.
10. Hashimoto, T., Shibayama, M. and Kawia, H., *Macromolecules*, 1983, **16**, 1093.
11. Hashimoto, T., Kowsaka, K., Shibayama, M. and Suehiro, S., *Macromolecules*, 1986, **19**, 750.
12. Hashimoto, T., Kowsaka, K., Shibayama, M. and Kawai, H., *Macromolecules*, 1986, **19**, 754.
13. Koch, M. H. J. and Bordas, J., *Nucl. Instrum. Methods*, 1983, **208**, 461.
14. Boulin, C. J., Kempf, R., Gabriel, A. and Koch, M. J. H., *Nucl. Instrum. Methods*, 1988, **A296**, 312.
15. Leibler, L., *Macromolecules*, 1980, **13**, 1602.
16. Han, C. D., Baek, D. M., Sakurai, S. and Hashimoto, T., *Polym. J.*, 1989, *21*, 841.
17. Han, C. D., Baek, D. M. and Kim, J. K., *Macromolecules*, 1990, **23**, 561.
18. Winter, H. H., Scott, D. B., Gronski, W., Okamoto, S. and Hashimoto, T., *Macromolecules*, 1993, **26**, 7236.
19. Owens, J. N., Gancarz, I. S., Koberstein, J. T. and Russel, T. P., *Macromolecules*, 1989, **22**, 3380.
20. Koberstein, J. T., Russel, T. P., Walsh, D. J. and Pottick, L., *Macromolecules*, 1990, **23**, 877.
21. roe, R.-J., Fishkis, M. and Chang, J. C., *Macromolecules*, 1981, **14**, 1091.
22. Floudas, G., Pakula, T., Fischer, E. W., Hadjichristidis, N. and Pispas, S., *Acta Polym.* 1994, **45**, 176.
23. Reynders, K., Soenen, H., Liskova, A., Berghmans, H. and Overbergh, N., *Macromolecules*, in preparation.
24. Mathot, B. F., *Calorimetry and Thermal Analysis of Polymers*. Carl Hanser Verlag, München, Vienna, New York, 1994.