Journal of Thermal Analysis and Calorimetry, Vol. 89 (2007) 2, 393–398

THE UTILIZATION OF TG/GC/MS IN THE ESTABLISHMENT OF THE MECHANISM OF POLY(STYRENE) DEGRADATION

Bob A. Howell[*]

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859-0001, USA

General purpose poly(styrene) is a large volume commodity polymer used in a variety of applications. It is widely used in food packaging, particularly for baked goods. In this application, the presence of styrene monomer, which has a distinctive taste and aroma, cannot be tolerated. Processing of the polymer and forming of the food container at an unacceptably high temperature leads to the formation of styrene monomer and finished articles with unacceptable aroma characteristics.

An examination of the thermal degradation of poly(styrene) has revealed the origin of monomer formation. The thermal decomposition of poly(styrene) has been widely studied. However, most studies have been carried out at high temperature (>300°C) where many processes are occurring simultaneously. Degradation at lower temperature, 280°C, occurs in two well-defined steps. The first is thermolysis of a head-to-head bond present in the mainchain as a consequence of polymerization termination by radical coupling. This generates macroradicals which smoothly depolymerize to expel styrene monomer. The nature of the degradation is readily apparent from kinetic analysis of the isothermal thermogravimetry (TG) data and the identity of the single volatile product may be readily established by gas chromatography/mass spectrometry (GC/MS) analysis of the effluent from the TG analysis.

Keywords: *defect structures, degradation mechanism, fully head-to-tail poly(styrene), poly(styrene) degradation, poly(styrene) microstructure, thermal stability*

Introduction

Poly(styrene) is a large volume, commodity polymer with a broad range of uses from automobile head light covers to inexpensive wine tumblers to food packaging. For use in food packaging the level of monomer in the finished article must be very low. Styrene monomer has a low taste and aroma threshold and the presence of even trace amounts in a food item will detract from its overall attractiveness. The processing of poly(styrene) for the formulation of packaging materials invariably involves some thermal treatments. It has long been known that poly(styrene) undergoes thermal degradation at relatively modest temperatures [1]. This degradation has been much studied [2]. An early study in which volatile evolution and molecular-mass changes during decomposition were monitored provided considerable insight [3, 4]. On the basis of molecular-mass changes with time of heating, it was concluded that an initial rapid drop in chain length is due to scission at a number of weak points distributed randomly along the polymer chains. However, the idea of random degradation was rejected for a number of reasons. First, a plot of (molecular mass)$^{-1}$ *vs.* time, which should be linear for a simple random degradation, showed rapid departure from linearity, suggesting that the initial rate at which bonds are broken is not sustained. Second, the molecular-mass distributions of degraded material were narrower than a random degradation would generate. Third, more monomer was produced than would be expected for random chain scission and fourth, the energy of activation was lower than anticipated. It was suggested that the initial high rate of volatilization is due to depropagation initiated at unstable chain ends produced by scission of weak links. Head-to-head linkages which might be more prone to scission than the typical head-to-tail links are introduced into the polymer mainchain by polymerization termination by radical coupling. The suggestion that the degradation of poly(styrene) is initiated at head-to-head links gained some support from the observation that the degradation of similar polymer produced by anionic techniques (no termination by coupling) is apparently the result of random chain scission [5, 6]. A plot of (molecular mass)$^{-1}$ *vs.* time for the degradation of this polymer is linear. Other studies have provided mixed results and have led to the suggestion that, under some conditions, processes other than chain scission, e.g., hydrogen atom transfer, make important contributions to the degradation [7–13]. The inconsistency in results arose from a number of factors including different temperatures (often high) utilized for decomposition,

---

[*] bob.a.howell@cmich.edu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

decomposition carried out in the presence or absence of oxygen, differences in the thermal history of the polymer samples used, and a lack of uniformity with respect to the methods of preparation/purification of the polymers subjected to degradation. In general, degradation studies have been carried out at the temperatures (>300°C) at which numerous fragmentation processes are occurring simultaneously such that it has not been possible to detail any process in a substantial manner [14–16]. Examination of the degradation over a range of isothermal temperatures from relatively low (280°C) to high (350°C) has revealed that at modest temperature the primary process (effectively the only process) which occurs is chain scission at a head-to-head unit present in the polymer as a consequence of polymerization termination by radical coupling followed by rapid expulsion of styrene monomer from the macroradicals thus formed. This may be readily demonstrated using thermogravimetry coupled with evolved gas analysis by gas chromatography/mass spectrometry.

Experimental

Materials and methods

Polymers

Atactic general purpose poly(styrene) was obtained by azo initiated radical polymerization of styrene in benzene at 60°C [16, 17]. Head-to-head poly(styrene) was obtained by hydrogenation of poly(2,3-diphenyl-1,3-butadiene) [16]. Fully head-to-tail poly-(styrene) containing no head-to-head units was obtained by nitroxyl-mediated radical polymerization of styrene followed by reductive removal of the nitroxyl end groups [6]. Poly(styrene) produced by anionic polymerization was purchased from Showa Denko K.K.

Instrumentation

Polymers were characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained in deuterochloroform using a General Electric QE-300 spectrometer. Infrared spectra were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs using a model 560 Nicolet MAGN-IR spectrophotometer. Molecular masses of the polymers were routinely determined by size exclusion chromatography (SEC) using solutions in THF, microstyrogel columns, and linear poly(styrene) calibration. For branching studies, solutions were prepared at a concentration of 1 mg mL^{-1} in THF and filtered through a 0.2 μm PTFE filter. The injection volume was 50 mL. THF was used as eluant at 1 mL min^{-1}. Separation was accomplished with three mixed bed columns (Polymer Laboratories) in series. For detection a Viscotek model H-502 differential viscometer was used in series with a Waters 2410 differential refractive index detector. Columns and detectors were held at 35°C. Narrow distribution poly(styrene) standards (Polymer Laboratories) were used to generate the universal calibration curve. Polystyrene 1683, a broad, linear poly(styrene) standard was used to verify system performance. The glass transition temperature (T_g) of polymers were determined using differential scanning calorimetry (DSC) at a heating rate of 10°C min^{-1}, using a TA Instruments Inc., Thermal Analyst model 2100 system equipped with a model 2910 MDSC cell. The sample compartment was subject to a constant purge of dry nitrogen at 50 mL min^{-1}. The thermal degradation characteristics were examined by thermogravimetry using a TA Instruments model 2950 TG unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The sample size was approximately 5–10 mg in a platinum sample pan. The temperature was ramped at a rate of 2 or 10°C min^{-1}. For isothermal kinetic studies the temperature was held at a specific temperature between 280 and 350°C. Mass loss was recorded as a function of time. Evolved gas analysis was accomplished using a Thermo Cahn TG-2131 microbalance in conjunction with a Thermo Finnegan TRACE GC/MS instrument. Approximately 2 mg of sample contained in platinum sample pan was placed in the furnace. The furnace compartment was purged with helium at a flow rate of 50 mL min^{-1} for 20 min prior to analysis. The temperature of the furnace was ramped from 25°C to the set point (280, 320, 350°C) at 10°C min^{-1} and held at the set temperature for 60 min. For the TG/MS analysis, the TG transfer line was maintained at 250°C in the GC oven. The mass spectrometer was operated in the electron impact mode using 70 eV electrons for ionization. The detector was maintained at 400 V. During the TG/MS experiment, a portion of the volatiles were collected in a cryotrap which was maintained at –100°C. After the TG/MS experiment was complete, the GC oven was cooled to ambient temperature and analysis of the mixture of volatiles in the cryotrap initiated. The column used was a Restek Corporation RTX-5MS of 15 m length and 0.25 mm internal diameter with a film thickness of 0.25 micron. The temperature program used was 40°C for 2 min and then 40 to 330°C at 10°C min^{-1}. Programmed flow was used for the helium carrier gas.

The flow was maintained at 4.5 mL min^{-1} for the first 4.5 min to maximize the amount of analyte pushed onto the column from the cryotrap. After that, the flow was reduced to 1.5 mL min^{-1} for the remainder of the analysis.

Results and discussion

The thermal degradation of poly(styrene) often limits the processing window for the polymer and can lead to the introduction of unacceptable levels of monomer in finished articles, particularly those used in food packaging. Although the degradation has been much studied, a full understanding of the processes which occur has not been available owing, in the main, to the decomposition being examined as a function of increasing temperature or at high temperature (>300°C). Under either of these conditions many processes occur simultaneously. To better understand the degradation several poly(styrene)s have been examined by TG with the volatile effulent from the decomposition being analyzed by gas chromatography/mass spectrometry (GC/MS). These include general purpose atactic poly(styrene) produced by conventional radical polymerization, a fully head-to-head poly(styrene) generated by hydrogenation of poly(2,3-diphenyl-1,3-butadiene), poly(styrene) containing no head-to-head units generated by nitroxyl-mediated radical polymerization of styrene followed by reductive removal of the nitroxyl end groups, and poly(styrene) produced by anionic techniques. The latter two polymers contain no head-to-head units as a consequence of the means of polymerization. The material from conventional radical polymerization contains one head-to-head unit as a consequence of polymerization termination by radical coupling [18]. The remaining polymer contains only head-to-head units.

A kinetic plot for the thermal degradation of general purpose poly(styrene) at 280°C is shown in Fig. 1. As may be noted two major processes are apparent. An initial early process is followed by a second which is much more rapid. Data for the early portion of degradation are replotted in Fig. 2. The rate constant determined from the slope of this plot is $4.15\cdot10^{-6}$ s^{-1} This is almost identical to the rate constant ($3.49\cdot10^{-6}$ s^{-1}) for the thermal degradation of the fully head-to-head polymer which is linear over the entire range of degradation (Fig. 3). This suggests that the same process is occurring during initial degradation of both polymers, i.e., the initial degradation of general purpose poly(styrene) containing a single head-to-head unit as a consequence of polymerization termination by radical coupling is identical to that of the fully head-to-head polymer. This is likely mainchain scission at head-to-head units. The material produced by conventional radical polymerization contains one head-to-head unit per chain as a consequence of termination by radical coupling [18]. The fully head-to-head polymer, of course, contains multiple head-to-head linkages. Degradation over the full range of decomposition corresponds to the cleavage of head-to-head units with little formation of volatile products. That this is indeed the case is apparent from 1.) the observation that the molecular mass of the head-to-head polymer continues to decrease as degradation occurs and 2.) analysis of the effluent from degradation of the two polymers by GC/MS.

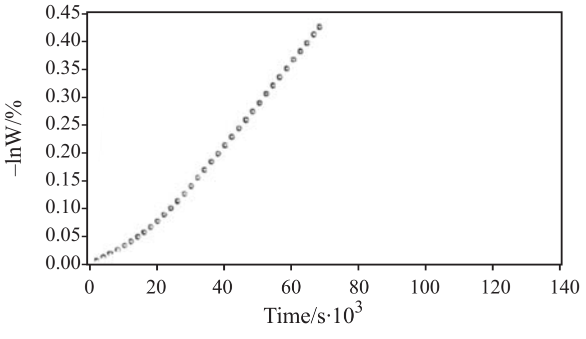

Fig. 1 Kinetic plot for the thermal degradation at 280°C of poly(styrene) produced by conventional radical techniques

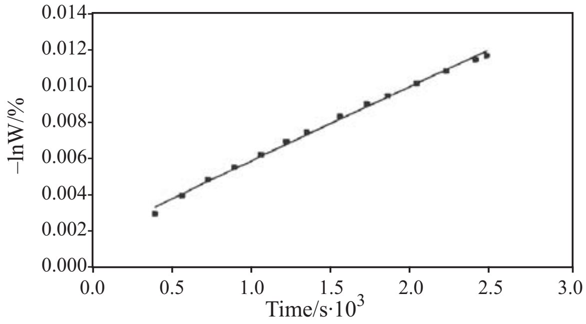

Fig. 2 Early portion of the kinetic plot for the thermal degradation at 280°C of poly(styrene) produced by conventional radical polymerization

Evolved gas analysis for the degrading polymers was conducted by thermogravimetry/mass spectrometry (TG/MS) and thermogravimetry/gas chroma-

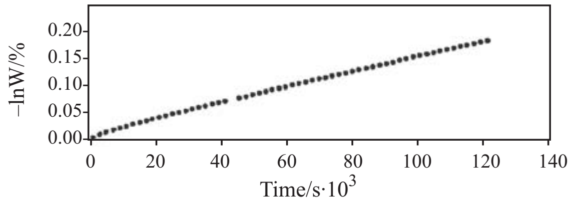

Fig. 3 Kinetic plot for the thermal degradation at 280°C of fully head-to-head poly(styrene)

tography/mass spectrometry (TG/GC/MS). In the first case, samples were held at 280°C for 80 min with any volatile fragments formed being carried by the helium purge gas to a mass selective detector tuned to *m*/*e* 104 (styrene monomer). For the head-to-head polymer no signal was detected nor was any measurable mass loss noted, i.e., the polymer was relatively mass stable at 280°C over the course of the experiment (it should be noted that the time at 280°C for this experiment was much shorter than that previously utilized for thermogravimetry at 280°C). In contrast, the conventional polymer lost 7.7% of its initial mass.

The TG/GC/MS experiments were even more revealing. The experiments were identical to those described above except that the volatiles formed from degradation of the polymer were carried onto the GC column prior to the mass selective detector. Again, the head-to-head sample lost very little mass at 280°C for 80 min. The behavior of the conventional polymer stands in sharp contrast to that of the head-to-head polymer. The TG/GC/MS chromatogram is shown below in Fig. 4. The only volatile compound formed from initial degradation of conventional poly(styrene) at 280°C is styrene monomer. For comparison, both chromatograms are shown in Fig. 5. It is clear in this comparison that while degradation of conventional poly(styrene) occurs when the polymer is subjected to 280°C for even a short time and that styrene monomer is evolved, the head-to-head polymer is relatively mass stable at this temperature and no styrene monomer is evolved. The results of the evolved gas analysis are fully consistent with those generated by thermogravimetry. They suggest that the thermal degradation of conventional poly(styrene), particularly at low temperature (<300°C), is initiated at head-to-head linkages present in the polymer as a consequence of polymerization termination by radical coupling. The macroradicals formed then undergo sequential unzipping to evolve styrene monomer.

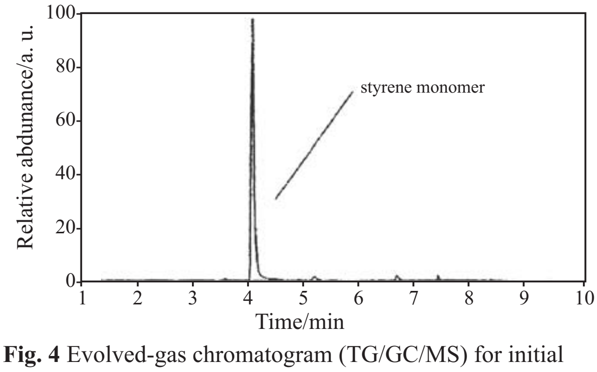

Fig. 4 Evolved-gas chromatogram (TG/GC/MS) for initial degradation of conventional atactic poly(styrene) at 280°C

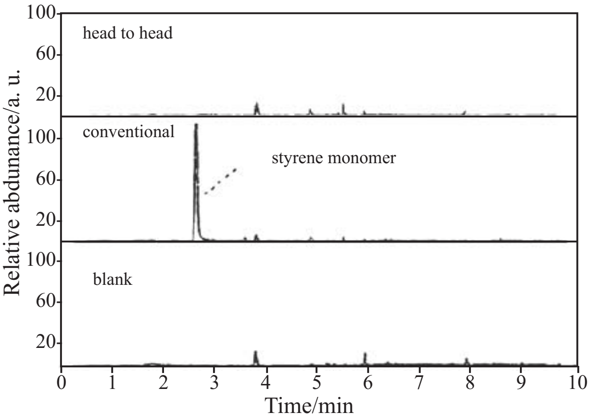

Fig. 5 Evolved-gas chromatograms (TG/GC/MS) for initial degradation of poly(styrene)s at 280°C

If the head-to-head linkage were not present the polymer should be much more thermally stable, i.e., the rapid evolution of styrene monomer at 280°C should not be observed. A fully head-to-tail polymer, i.e., a polymer containing no head-to-head units, was produced by nitroxyl mediated radical polymerization of styrene followed by reductive removal of the nitroxyl end groups [17]. A comparison of the degradation behavior of this polymer with that of conventional poly(styrene) is shown in Fig. 6. The fully head-to-tail polymer (no head-to-head units) is much more stable at 280°C, than the conventional polymer. As noted above, two different processes are involved in the decomposition of the conventional polymer. The initial reaction involves mainchain cleavage at head-to-head units to produce macroradicals which then evolve monomer at a rate much greater than that for the initial chain cleavage. On the other hand, degradation of the fully head-to-tail (no head-to-head units) polymer results from random mainchain cleavage with a rate constant of $8.70\cdot10^{-6}$ s^{-1}. Random chain scission is confirmed by a decrease in polymer molecular mass as a function of time (Fig. 7). At higher temperatures the decomposition behavior of

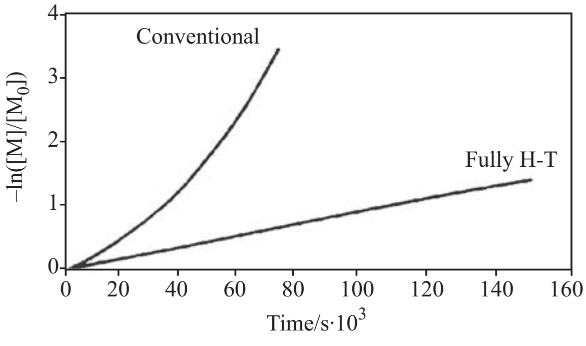

Fig. 6 Thermal degradation at 280°C of poly(styrene) containing no head-to-head units and poly(styrene) produced by conventional radical techniques

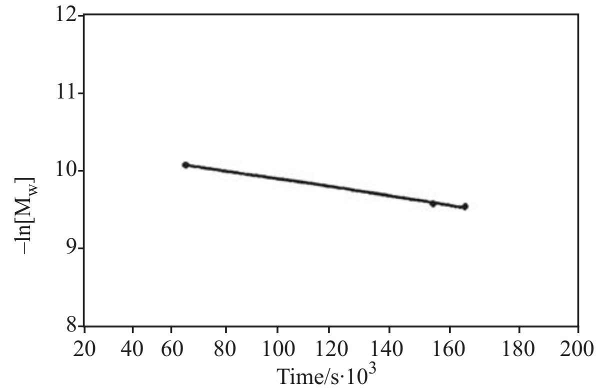

Fig. 7 Change in molecular mass of fully head-to-tail poly(styrene) as function of time at 280°C

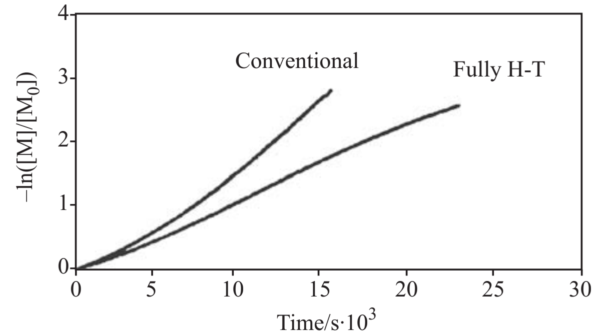

Fig. 8 Kinetic plots for thermal degradation of poly(styrene) containing no head-to-head units and general purpose poly(styrene) at 320°C

both polymers is more complex. Plots for degradation at 320°C are displayed in Fig. 8. When the decomposition temperature was raised to 350°C, the degradation characteristics of both polymers were very similar to those at 320°C. However, the degradation of conventional poly(styrene) was still much more rapid than that for the polymer containing no head-to-head units. At this temperature it is likely that several processes are occurring simultaneously, i.e., sufficient energy is available to bring about random chain scission in both polymers and structural differences are not as apparent as for degradation at lower temperatures.

Poly(styrene) produced by anionic polymerization contains no head-to-head units and should display stability greater than that observed for poly(styrene) generated by conventional radical techniques. A commercial polymer produced by anionic techniques was examined by thermogravimetry. The degradation characteristics for this material are very similar to those of poly(styrene) generated by nitroxyl mediated radical polymerization. For comparison kinetic plots are displayed in Fig. 9. Both polymers generated by methods that preclude the inclusion of a head-to-head unit in the mainchain are much more thermally stable than material produced by conventional radical techniques and containing one head-to-head unit per chain as a consequence of polymerization termination by radical coupling.

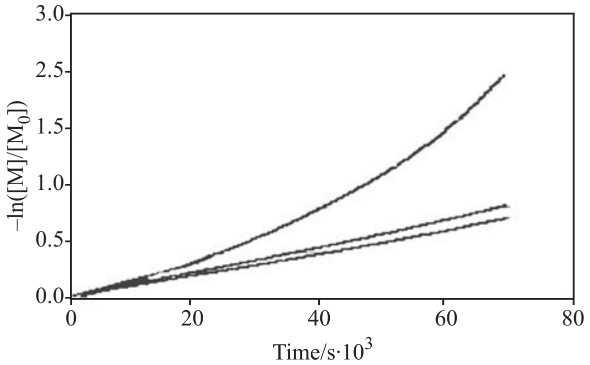

Fig. 9 Comparison of the thermal degradation of fully head-to-tail poly(styrene) produced by mediated radical polymerization (bottom line), head-to-tail poly(styrene) generated by anionic techniques (middle line) and general purpose poly(styrene) produced by conventional radical polymerization (top line)

Conclusions

It is apparent that the degradation of poly(styrene) produced by conventional radical polymerization, i.e., general purpose poly(styrene), at temperatures below 300°C is initiated by mainchain scission at a head-to-head unit present in the polymer as a consequence of polymerization termination by radical coupling. The macroradicals thus formed readily unzip to expel monomer so that the mass loss as a function of time is rapid. The rapid loss of mass is apparent from thermogravimetry and the identity of styrene monomer as the single entity being lost has been demonstrated by evolved gas analysis. In contrast, a fully head-to-tail poly(styrene) prepared by nitroxyl-mediated polymerization of styrene monomer followed by removal of the nitroxyl end groups by a reductive technique is much more thermally stable than the corresponding polymer prepared by conventional radical polymerization. Degradation corresponds to random mainchain scission to form oligomers as opposed to the expulsion of monomer as observed for the conventional polymer. Similar behavior is exhibited by head-to-tail poly(styrene) generated by anionic techniques.

References

1 H. Staudinger and A. Steinhofer, Ann., 571 (1935) 35.
2 N. Grassie and G. Scott, 'Polymer Degradation and Stabilization', Cambridge University Press, Cambridge, UK 1985.
3 H. H. F. Jellinek, J. Polym. Sci., 3 (1948) 850.
4 H. H. F. Jellinek, J. Polym. Sci., 4 (1948) 13.
5 G. G. Cameron, W. A. J. Bryce and I. T. McWalter, Eur. Polym. J., 6 (1984) 563.
6 B. A. Howell, Y. Cui, K. Chaiwong and H. Zhao, J. Vinyl Add. Tech., 12 (2006) 198.
7 N. Grassie and W. W. Kerr, Trans. Faraday Soc., 53 (1957) 249.
8 N. Grassie and W. W. Kerr, Trans. Faraday Soc., 55 (1959) 1050.
9 S. L. Madorsky, J. Polym. Sci., 9 (1952) 133.
10 S. L. Madorsky, D. McIntyre, J. H. O'Mara and S. Straus, J. Res. Natl. Bur. Std., 66A (1962) 307.
11 S. L. Madorsky and S. Straus, J. Res. Natl. Bur. Std., 40 (1948) 417.
12 O. Chiantore and M. Guaita, Polym. Degrad. Stab., 12 (1985) 141.
13 M. Guaita, Britsh Polym. J., 18 (1985) 226.
14 H. Inoue, M. Helbig and O. Vogl, Macromolecules, 10 (1977) 1331.
15 I. Luederwald and O. Vogl, Macromol. Chem., 180 (1979) 2295.
16 B. A. Howell, Y. Cui and D. B. Priddy, Thermochim. Acta, 396 (2003) 167.
17 B. A. Howell and K. Chaiwong, 'Thermal Stability of Poly(styrene) Containing no Head-to-Head Units', Proceedings, 33rd Annual Meeting of the North American Thermal Analysis Society, 2005.
18 D. R. Hensley, S. D. Goodrich, A. Y. Huckstep, H. J. Harwood and P. L. Rinaldi, Macromolecules, 28 (1995) 1586 and references cited therein.

DOI: 10.1007/s10973-006-8152-7