

## Solvents for thermoporosimetry analysis of natural rubber networks

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**ABSTRACT:** Thermoporosimetry is known as an analytical method to investigate network structures in swollen elastomers. Despite this interesting potential capability, only few investigations are published in literature which apply different solvents on differently crosslinked natural rubber samples. The choice of the solvent is critical as it strongly influences the separation of confined and bulk solvent transition signal, the confined solvent signal intensity and the peak width representing the pore size resolution. No critical comparison has been done in these investigations regarding the solvent choice related to peak separation, pore size resolution or signal intensity. Furthermore, no critical assessment is available relating thermoporosimetry results to solvent parameters to identify an optimal solvent regarding the mentioned criteria. This argument motivated the present investigation to identify the most appropriate solvents for the analysis of natural rubber compounds by thermoporosimetry. Different types of solvents (aliphatic, aromatic, non-polar, and polar) were selected and benchmarked against each other. It was concluded that n-heptane was identified as the best solvent for these investigations. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43998.

**KEYWORDS:** differential scanning calorimetry (DSC); elastomers; rubber; swelling

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### INTRODUCTION

The pore structure characterization of materials based on the shift in the thermal transition point of a liquid is called thermoporosimetry.<sup>1–5</sup> Differential scanning calorimetry (DSC) is applied to measure thermodynamic differences between confined and free solvent. The pore structure is then related to the confined solvent information. In general, two different experimental approaches are known: freezing point depression (FPD) or melting point depression (MPD). Freezing point depression experiments are influenced by the crystallization kinetics.<sup>6</sup> Melting point depression studies follow the thermodynamically less complex process of melting and are thus the approach of choice in the present study.

The measured difference in the solid-to-liquid phase transition temperature of a confined solvent ( $\Delta T$ ) depends on its environment and changes with the cavity parameters [pore size ( $r_p$ ), surface tension ( $\gamma_{SL}$ ), contact angle ( $\theta$ )] and is often described according to the basic Gibbs–Thomson equation<sup>1</sup>:

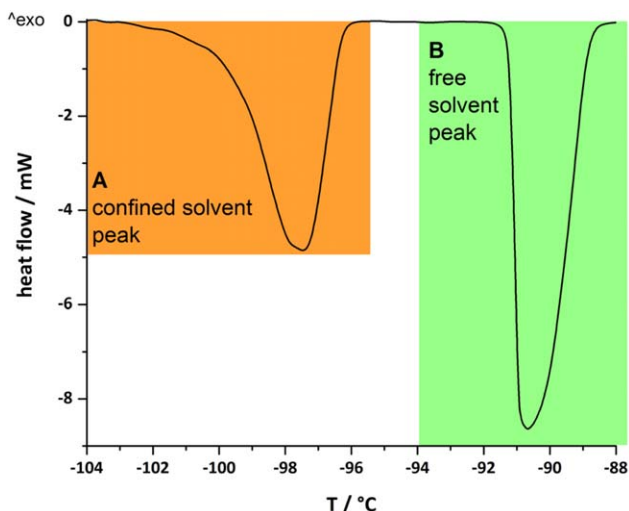
$$\Delta T = \frac{4 * \gamma_{SL} * \cos \theta * T_0}{r_p * \Delta H_f * \rho_S} \quad (1)$$

where  $T_0$  is the melting temperature of the free solvent and  $\Delta H_f$  is the heat of fusion of the used solvent associated to the pure solvent,  $\rho_S$  is the crystal density of solvent crystals. Standard

thermoporosimetry is typically applied on hard porous materials like silica,<sup>7,8</sup> carbon black,<sup>9</sup> or cement.<sup>10</sup> Only a few studies investigating the pore structure of polymeric compounds like polysiloxanes,<sup>11</sup> polyamides,<sup>12</sup> collagens,<sup>13</sup> cellulose,<sup>14,15</sup> polyolefines,<sup>16</sup> or natural rubber<sup>17</sup> have been reported. When analyzing such polymeric materials, the Gibbs–Thomson eq. (1) has to be extended<sup>2–4,18,19</sup> in order to account for the solvent–polymer interaction via the Flory–Huggins thermodynamics theory:<sup>20–24</sup>

$$\left( \frac{1}{T} - \frac{1}{T_0} \right) \left( \frac{\Delta H_f}{R} \right) = - \left\{ \ln(1 - V_r) + \left[ 1 - \left( \frac{1}{x} \right) \right] * V_r + \chi * V_r^2 \right\} \quad (2)$$

where  $V_r$  is the volumetric fraction of polymer,  $x$  is the degree of polymerization, and  $\chi$  is the polymer–solvent interaction parameter. Different models are discussed in the literature which combine the basic Gibbs–Thomson eq. (1) with different aspects of polymer physics for the network structure characterization of polymeric compounds.<sup>20–29</sup> In these studies, various solvents were used to get structural information about the samples.<sup>16,17,30–38</sup> The present work reports thermoporosimetry data for different solvents used on a NR model compound. The influence on the thermodynamic behavior of confined solvent in the rubber matrix is characterized by DSC measurements of the heat flow. The results are traced back to polymer and



**Figure 1.** Schematic thermogram with assignment of confined/pore (A) and free/bulk (B) solvent signal. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

solvent parameters to facilitate the identification of ideal solvents for the thermoporosimetry investigation of natural rubber compounds in equilibrium swollen state.

## EXPERIMENTAL

### Sample Preparation

The natural rubber compound was mixed with 3 parts per hundred of rubber (phr) of zinc oxide, 1 phr of sulfur (S), 3 phr of N-cyclohexyl-2-benzothiazolesulfenamide (CBS), 2.5 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD), and 1 phr of stearic acid in a laboratory two-roll mill. The used CBS/S ratio favors an efficient cure system. The rubber compound was vulcanized at 150 °C for 16.5 min until 90% of the maximum torque was reached, according to the rheometer experiment. Samples were swollen until equilibrium (18 h), cut to loosely fit into the DSC crucibles and sealed hermetically.

### DSC Measurements

The DSC measurements were carried out on a DSC 1/500 system from Mettler-Toledo with a HSS8 temperature sensor. DSC crucibles from Mettler-Toledo were used for the thermoporosimetry measurements (Al-crucibles 40  $\mu$ L without pin, ME-51119870). The investigated solvents were purchased from Sigma-Aldrich (analytical grade) and were used without further purification.

The heating rate (HR) and the temperature profile were both adapted to the specific solid–liquid transition point of the solvent. The results of the investigated solvents revealed that a high heating rate is required to increase the sensitivity, whereas slower scan rates are required for improving the resolution between the melting peaks. Consequently, a low scanning rate is essential to obtain a baseline resolution for large pores.<sup>39</sup> In the thermograms, two phase transitions were observed: The peak at a lower temperature represents the phase transition of solvent confined in the elastomer network and the second one at higher temperature shows the transition of the bulk solvent (see Figure 1).

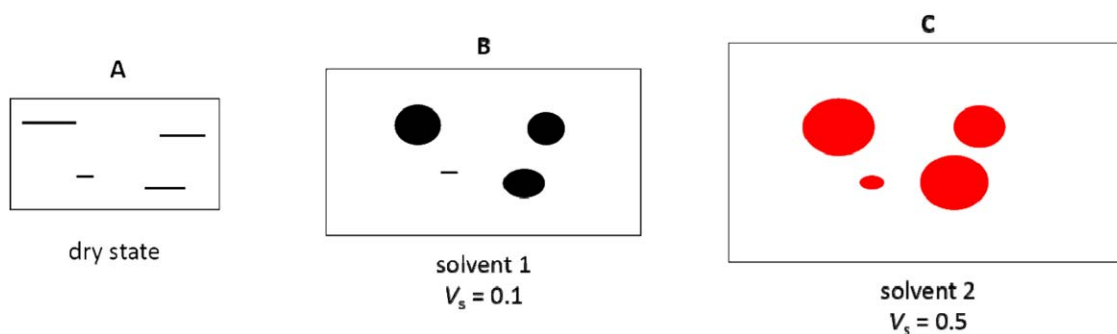
Thus, for each studied solvent, the heating rates were optimized to achieve the best possible resolution of bulk and pore solvent transition as well as a good peak intensity considering reasonable measurement times.

## RESULTS AND DISCUSSION

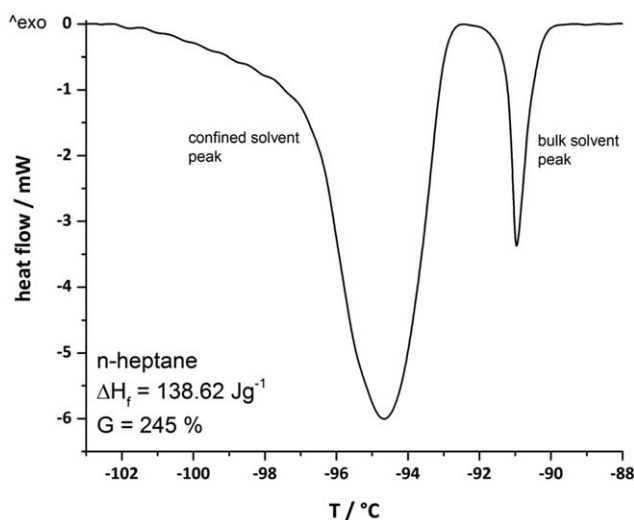
The literature mainly reports water as solvent for thermoporosimetry analysis of hard porous materials.<sup>40–43</sup> This solvent cannot be applied on natural rubber compounds because water, as a polar solvent, has a low affinity to the non-polar polymer. The missing interaction restricts the incorporation of water into the polymeric structure. Consequently, the surface tension is very high leading to a small contact angle. The sharp contact angle and the high surface tension induce a bad wettability of the pore which restricts thermoporosimetric investigations. In the present study, the network analysis of the NR model compound was conducted using different type of organic solvents:

- Linear alkanes<sup>44–48</sup>: odd and even numbered
- Aromatics<sup>16,30,33</sup>: toluene, xylene
- Cyclic hydrocarbons<sup>11,21,36,47,49,50</sup>: cyclohexane
- Cyclic ethers<sup>39</sup>: 1,4-dioxane

Acetone was not applied on the NR sample because of its high polar character and its low swelling ratio. Furthermore, halogenated solvents were excluded from the present study due to their possible environmental incompatibility. Every investigated solvent leads to a differently formed pore transition peak depending on the volume of the solvent included in the polymer, the enthalpy of fusion and the Flory–Huggins solvent–polymer interaction parameter. In dry state, no solvent is included in the polymer and the network structure is not expanded [Figure



**Figure 2.** Schematic visualization of the pore size sensitivity. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** Thermoanalysis of natural rubber sample swollen with n-heptane (HR: 0.7 °C/min).

2(A)]. Mixing the polymer with a solvent, the liquid penetrates into the polymeric network because of the osmotic pressure. The polymer strands are stretched and give an elastic response to the solvent uptake until osmotic pressure and elastic response are equal. The condition is called equilibrium swelling state, the volume ratio of solvent ( $V_s$ ) quantifies the amount of solvent in the polymer–solvent mixture and the expansion factor  $G$  the relative increase of mass due to solvent uptake. If the same pore (e.g., the mesh size in rubber networks) is analyzed by two different solvents, two different temperature depressions will be determined. These values are related (among other factors) to the different sizes and cavity parameters depending on the Flory–Huggins polymer–solvent interaction parameter. The higher expansion of the elastomer leads to an increase of the pore radius and increases the solvent volume. This change is proportional to the temperature difference according to the Gibbs–Thomson eq. (1). In an extreme case where very small pores are present, the solvent–polymer interaction promotes lower osmotic pressure that could not be enough to enlarge the solvent volume in these cavities with higher elastic response [Figure 2(B)]. In a thermoporosimetry analysis, no signal would be generated because of the lack of solvent in those pores. If a second solvent with a higher affinity to the rubber matrix is used, an increase of the solvent volume in the pores is observed due to a higher expansion of the elastomer because of the increment of the osmotic pressure. As consequence, these small pores could be filled with the solvent and they could be detected in the thermoporosimetry experiment [Figure 2(C)]. The pore size sensitivity is consequently enlarged by using better solvents leading to a higher, filled pore volume.

#### n-Heptane

In the past, n-heptane was successfully used in thermoporosimetry analysis of crosslinked EPDM elastomers by Baba *et al.*<sup>44</sup> In the current work, the thermoporosimetry investigations of the n-heptane as swelling solvent for NR samples show a good separation of pore and bulk solvent signal, a good melting peak resolution with short measurement times (Figure 3). The signal

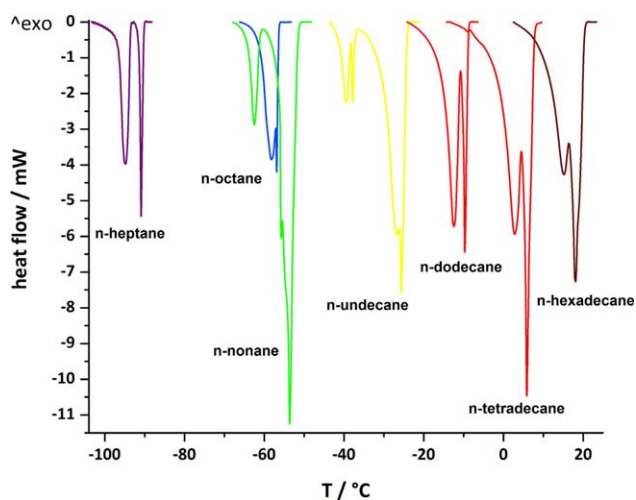
intensity of the confined solvent is high compared with other tested solvents (see below), which should be related with the enthalpy of fusion, which specifies the amount of heat flowing into one gram of a substance during a melting or freezing event. For n-heptane, 138.62 J heat per gram of solvent are transferred from the heater to the sample, whereas 72.02 J/g is measured for toluene. Thus, for the same amount of solvent the heat flow associated to the freezing or melting transition of n-heptane will be approximately twice as high as in the case of toluene, according to the standard enthalpy of these processes.<sup>45</sup>

According to these statements, n-heptane appears as a suitable solvent candidate for thermoporosimetry investigations of cross-linked NR compounds, being only limited by its low melting temperature.

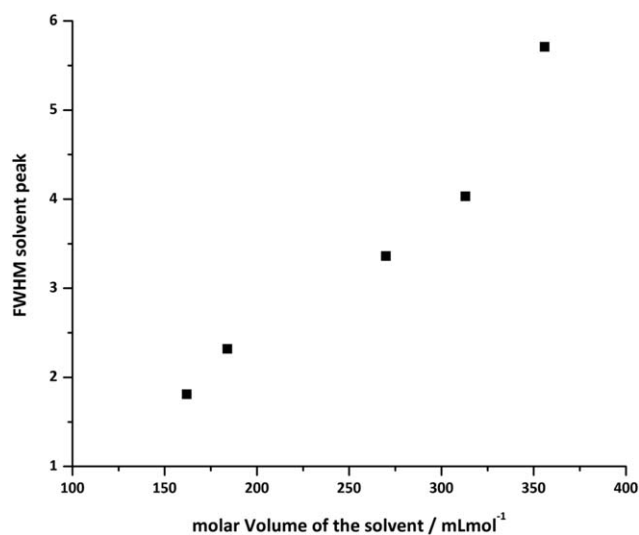
#### Longer n-Alkanes

In order to shift the detection window to higher temperatures maintaining similar resolution characteristics, the use of longer chain alkanes has been investigated. N-octane and n-dodecane show similar  $\chi$  parameters<sup>51</sup> as n-heptane with higher enthalpy of fusion, leading to a higher peak intensity [ $\Delta H_f$ (n-heptane) = 138.62 J/g;  $\Delta H_f$  (n-octane) = 181.56 J/g;  $\Delta H_f$  (n-dodecane) = 216.25 J/g].<sup>52</sup> In the literature, alkanes containing 6, 7, 10, 12, and 16 carbon atoms were shown to be acceptable solvents for the study of silica samples as well as partially swollen, non-crosslinked NR systems.<sup>20,30</sup> For the vulcanized NR sample characterized in the present study, these results could not be confirmed (see Figure 4).

The different alkanes from n-octane to n-hexadecane show overlapping signals of the solvent transitions. The overlap of the individual peaks increases with chain length which is related to a broadening of the pore melting peak, mainly caused by the increasing molar volume of the solvents.<sup>53</sup> Thus solvents with higher molar volume will enlarge the pore size and consequently the shifting of the pore solvent transition with respect to the bulk solvent is reduced. This correlation can be visualized



**Figure 4.** Thermogram overview of natural rubber sample investigated with different odd and even n-alkanes (HR: 0.5 °C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** FWHM of the pore melting peaks from even alkanes in natural rubber with increasing molar volume.

by comparison of full width half maximum (FWHM) of the pore peak (Figure 5). The values were calculated fitting the pore peaks with a Gaussian function (Peak Analyzer, OriginPro 2015).

Linear hydrocarbons with an odd number of atoms were not considered in former thermoporosimetry studies because a solid-rotator transition<sup>45,48</sup> was observed. This change in molecular orientation occurs directly after freezing/melting and increases with the alkane chain length (Figure 4). N-nonane reveals such a transition only in bulk solvent as small additional peak. If n-undecane is used as solvent, the transition is more intensive and visible in both solvent signals (Figure 4). According to literature, all further linear odd alkanes exhibit an order-disorder transition from C9 to C37.<sup>46</sup> Such transitions were likewise observed for even alkanes from C22 up to C44.<sup>46</sup>

Among the used linear hydrocarbon solvents, n-hexane could be a further possible candidate but was excluded because of its lower solid-liquid transition temperature compared with n-heptane. Out of the analysis of different alkanes it could be con-

cluded that n-heptane is the best linear alkane, for the efficient pore size determination of crosslinked rubber compounds with thermoporosimetry.

#### Aromatic Solvents

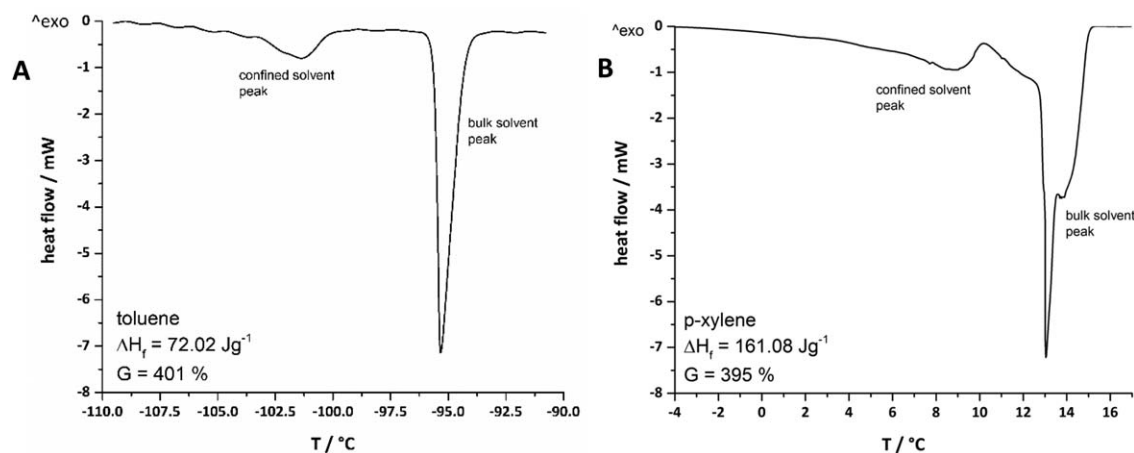
Aromatic solvents have been investigated because they are better solvents (from a thermodynamic point of view) for natural rubber in terms of  $\chi$  parameter.<sup>51</sup> Compared with linear alkanes, toluene shows a broader pore transition peak accompanied by a reduced intensity [Figure 6(A)].

The reduced pore solvent signal intensity might relate to a reduced enthalpy of fusion of toluene compared with n-heptane, whereas the broader melting peak arises from a change in polymer swelling behavior [ $G(\text{toluene}) = 401\%$ ;  $G(\text{n-heptane}) = 245\%$ ]. Thus, toluene shows a higher expansion of the pores compared to n-heptane, which results in an increased pore size sensitivity. The enhanced pore size sensitivity favors toluene for investigations but the reduced signal intensity impedes data evaluation. Consequently, toluene is not recommended as solvent for the standard application in thermoporosimetry of NR samples but should potentially be used if the pore size sensitivity is insufficient.

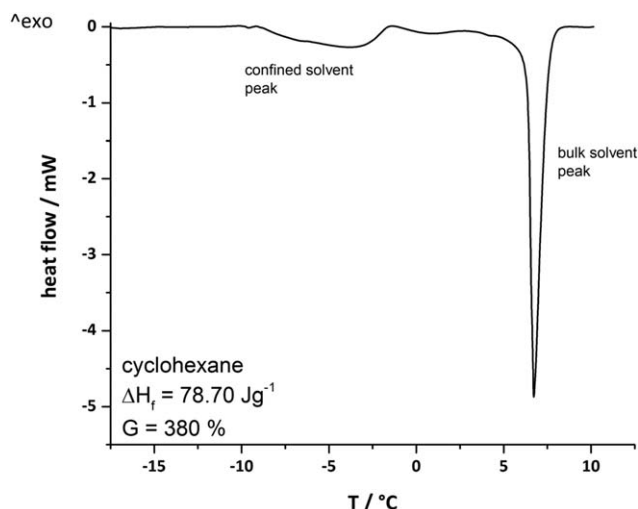
A second possible aromatic solvent with a higher enthalpy of fusion as toluene or n-heptane is p-xylene [Figure 6(B)]. The higher enthalpy of fusion combined with a high swelling ratio favors the use of p-xylene because a broad and intense pore melting peak could be expected [ $\Delta H_f(\text{toluene}) = 72.02 \text{ J/g}$ ;  $\Delta H_f(\text{p-xylene}) = 161.08 \text{ J/g}$ ;  $G(\text{toluene}) = 401\%$ ;  $G(\text{p-xylene}) = 407\%$ ].<sup>52</sup> Unfortunately, pore and bulk solvent peak cannot be completely separated. Therefore, p-xylene is not recommended as solvent for pore size determination.

#### Cyclohexane

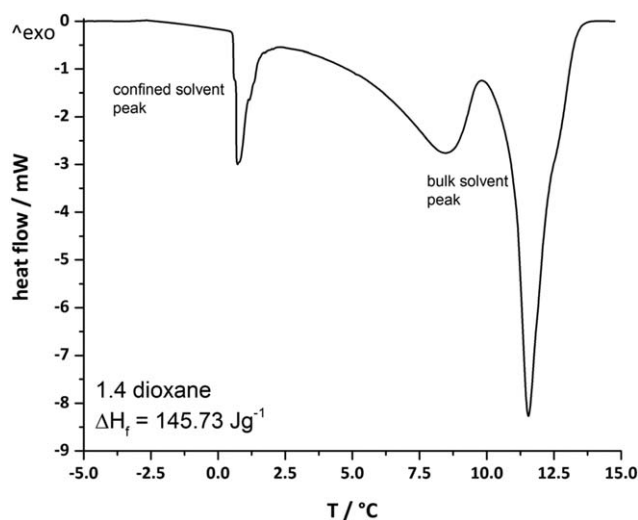
The best separation of bulk and pore transition signal is achieved using cyclohexane (Figure 7). The pore solvent signal is as broad as in the case of toluene which is related to a similar swelling ratio [ $G(\text{toluene}) = 401\%$ ;  $G(\text{cyclohexane}) = 380\%$ ]. Consequently, the pore size sensitivity of cyclohexane is comparable to those obtained with toluene, but at higher melting temperature. The enthalpies of fusion of both solvents are also very similar [ $\Delta H_f(\text{toluene}) = 72.00 \text{ J/g}$ ;  $\Delta H_f(\text{cyclohexane}) = 78.70 \text{ J/g}$ ]<sup>52</sup> which is visualized in the thermograms: both solvents only show



**Figure 6.** Thermoanalysis of natural rubber sample with (A) toluene (HR: 1°C/min) and (B) p-xylene (HR: 0.5°C/min).



**Figure 7.** NR model compound investigated by using cyclohexane (HR: 0.5 °C/min).



**Figure 8.** Thermogram of natural rubber compound swollen in 1,4-dioxane (HR: 0.5 °C/min).

a weak pore signal [Figures 6(A) and 7]. Cyclohexane is not preferred for routine thermoporosimetry investigations because of its weak pore signal, which impairs exact data interpretation.

#### 1,4 Dioxane

1,4 dioxane is a polar candidate for the investigation of the pore structure of rubber compounds.

A known solid–solid transition of 1,4-dioxane is observed in the bulk melting peak (Figure 8). This transition limits pore size distribution determination of polymeric materials because of overlapping events. The solid–solid transition is even more visible analyzing standard silica samples. Therefore, 1,4-dioxane is not a good solvent for thermoporosimetry investigations.

#### CONCLUSIONS

Different types of solvents (aliphatic, aromatic, non-polar, and polar) were investigated for thermoporosimetry studies on sulfur crosslinked NR compounds.

N-heptane was identified as best solvent for these investigations. It shows high melting point depression and high transition energy. Only the expansion factor for equilibrium swelling is not as high as measured for aromatic solvents, leading to a reduced pore size resolution. Other candidates of this solvent class are not suitable for thermoporosimetry because of solid-rotator disorder (odd alkanes) or overlapping transition events because of the higher molar volume (even hydrocarbons).

Toluene and p-xylene were investigated as aromatic solvent candidates. Toluene shows a high network expansion in equilibrium swelling leading to a higher pore size resolution compared with n-heptane. Unfortunately, the low enthalpy of fusion leads to a small pore signal for natural rubber samples, which is not ideal for analysis. In the same line, p-xylene shows the same swelling ratio but exhibits a larger enthalpy of fusion compared with toluene. Unfortunately, the separation between pore and bulk solvent signal is not possible.

The highest separation between bulk and pore solvent is obtained by using cyclohexane. But like toluene, the pore solvent signal of cyclohexane shows a weak intensity which impairs the investigation of the NR system. This observation is again traced back to a lower magnitude of the enthalpy of fusion. Finally, 1,4-dioxane is also not suitable solvent for thermoporosimetry measurements in NR samples because of the overlapping of solid–solid transitions.

This study showed that three different solvents facilitate an efficient thermoporosimetry pore size analysis of a model NR compound. N-heptane is the solvent of choice for routine network structure investigations. Compared with toluene or cyclohexane the pore size resolution is reduced. Toluene and cyclohexane are alternatives to n-heptane in case a more detailed resolution of small changes in the pore size is required, taking into consideration the reduced signal intensity showed by these solvents.

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