Polymer Bulletin 9, 344–347 (1983)

Polymer Bulletin

DSC Evidence for Tu > Tm in n-Alkanes and Polymers

Comment to the Paper by P. Claudy and J.M. Létoffé "About the Transition of n-Alkanes Above the Melting Point", Poly. Bull. 9, 245 (1983)

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SUMMARY

We agree with Claudy and Létoffé that oxidation of hydrocarbons can occur in closed DSC pans because of entrapped O_2. We do not find oxidation in open pans under flowing N_2 unless dissolved O_2 is present in the polymer. We report a Tu > Tm in trans polyisoprene by DSC (open pan) and by dynamic mechanical loss. Our work supports the existence of the Tu transition of Krüger and coworkers.

DISCUSSION

Exothermic peaks observed with closed DSC pans above the melting points of n-alkanes are ascribed by Claudy and Létoffé (1) to oxidation and by Höhne (2) to a pressure induced ordering. Our own DSC studies (3) on n-alkanes and semi-crystalline polymers, conducted with open DSC pans under a stream of O_2 free N_2, showed only endothermic slope changes or step jumps whose temperatures we assigned as being the Tu > Tm transition of Krüger et al. (4,5). We have observed exothermic effects using both open and closed DSC pans with atactic polystyrenes which contained dissolved or entrapped atmospheric O_2 (6). It is known that PS experiences uncatalyzed thermal oxidation starting in the $T_{\ell\ell}$ = 1.2 Tg region and hence we routinely store PS specimens under vacuum, with minimal subsequent exposure to air (6).

The shapes of the exotherms in Figures 1 and 2 of Ref. (1) are consistent with an activated oxidation process which accelerates with temperature and then rapidly decelerates as the supply of O_2 is exhausted. There is a tendency in Figure 2 for the peak temperature to be higher the smaller the sample weight. In this case (1), as with ours for dissolved O_2 in PS (6), the ratio of hydrocarbon sample weight to available oxygen tends toward infinity.

Höhne (2) has suggested that our endothermic effects reported on n-alkanes using open DSC pans (3) were a result of evaporation of the n-alkanes. We had considered and rejected this possibility prior to publication on several grounds: 1) the tendency for Tu/Tm (K/K) to be close to 1.2; 2) boiling points, Tb, for n-alkanes start out with Tb/Tm ~ 2 and increase without limit; 3) mixed alkanes with 10-20% w/w of lower boiling alkanes gave the same Tu as did the higher boiling major constituent, using open pans; 4) experiment with closed pans gave the same Tu as with open pans. We did not observe either of the exotherms reported in (1) and (2).

A more rigorous test for artifacts is possible when two different methods give the same Tu. We reported (3) for a polywax 2000

($n \sim 142$) a Tu = 489K at a heating rate of 10 K $min.^{-1}$, 444 K at 0.5 K $min.^{-1}$ Kruger et al. (5) subsequently measured a PE of $\overline{M}n$ = 2200 by Brillouin scattering with Tu = 436 K. Such agreement could hardly be a coincidence. If each were the result of an artifact, the artifacts had to be quite different.

More recently we have found that gutta percha (trans polyisoprene) exhibits an unusually strong Tu by DSC at 416 K, giving a Tu/Tm of 1.25. We then examined this same specimen with the DuPont Dynamic Mechanical Analyzer, 981, at a frequency of 14 Hz. This test revealed a strong Tu on heating and again on cooling, using a special sample support technique developed by Keinath and Boyer (7). Figure 1 combines DSC and DMA traces on gutta percha. The latter shows a strong premelting ($T\alpha_c$) and weak Tm, followed by Tu, all at a heating rate of 5 K $min.^{-1}$. Tg was also observed at -38°C (235K), but is not shown here. Tu/Tm is again 1.25. Tu for this polymer is so intense that sensitivity did not have to be increased above Tm as was our practice in Ref. (3).

Our very first evidence of Tu by DSC was with a specimen of poly (4-methyl pentene-1) supplied to us by Krüger who had reported for it a Tu of 589 K by Brillouin scattering (4). Recent re-determinations with open DSC pans give Tu = 568, Tm = 502 for a ratio of 1.13. This Tu is beyond the upper working range of our DMA unit.

Our high sensitivity DSC studies support the Brillouin scattering results of Krüger et al. (4,5) and the kinematic viscosity results of Pietralla and Krüger (8). We now add dynamic mechanical analysis which thus far has been successfully employed only on trans PI. Other polymers such as the polyethyleneoxides and especially the n-alkanes, have proven to be too fluid in the melt for our technique (7).

REFERENCES

1. Claudy, P., Létoffé, J.M., Polymer Bulletin, in press.
2. Höhne, G.W.H., Polymer Bulletin, 4, 627 (1981).
3. Denny, L.R., Boyer, R.F., Polymer Bulletin, 4, 527 (1981).
4. Krüger, J.K. et al., Polymer, 21, 620 (1980).
5. Krüger, J.K. et al., Polymer Bulletin, 5, 615 (1981).
6. Denny, L.R. et al., J. Polym. Sci., in press.
7. Keinath, S.E., Boyer, R.F., J. Applied Polym. Sci., in press.
8. Pietralla, M. and Krüger, J.M., Polymer Bulletin 2, 663 (1980).

ADDED NOTE

We decided to duplicate the experiments of Ref. (1) with hermetically sealed pans using C_{30}, C_{36} and C_{40}, at a heating rate of 10 K min^{-1}, a high sensitivity setting of 0.1 mJ s^{-1} cm^{-1}. All three showed definite exotherms with the C_{30} and C_{40} being unusually strong. At the same time, we realized that the temperature at which oxidation commences is very close to our Tu values. See Table I. We suggest tentatively that smectic structure which Krüger postulates to be present at $T_u > T_m$ inhibits oxidation so that the oxidation reaction commences only near Tu. To check this point, C_{40} was heated in an open pan to above Tu in order to destroy structure. It was then cooled to below Tm and reheated in a sealed pan. This time, oxidation began at a lower temperature. We had noted previously (3) that Tu could not be observed on a second heating of n-alkanes. We subsequently demonstrated (in as yet unpublished experiments) that a prolonged waiting period of days to weeks at 20°C could restore Tu.

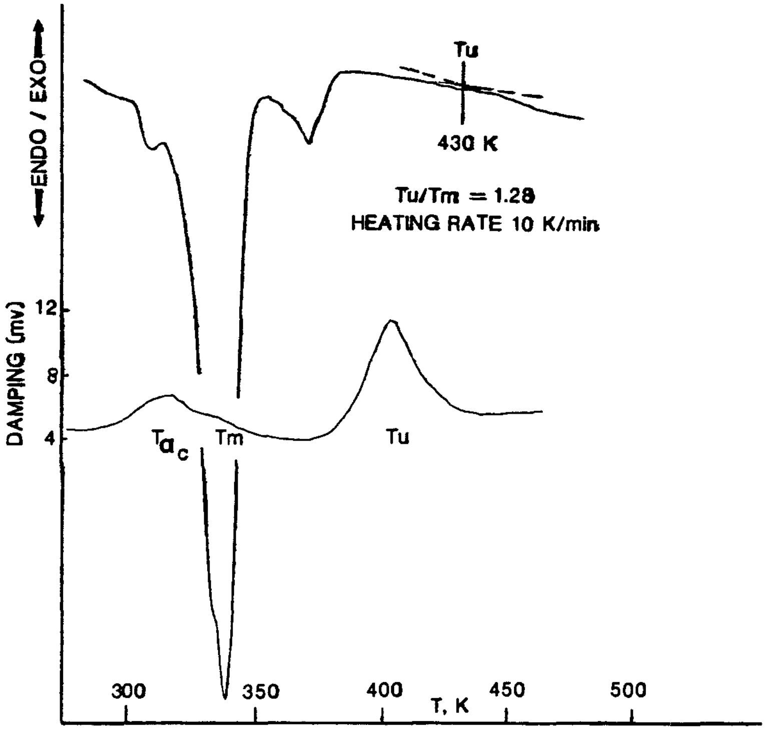

Figure 1. Top: DSC 0.1 mJ s^{-1} cm^{-1} trace on gutta percha. Sensitivity was not increased above Tm as practiced in Ref. (3). Bottom: Dynamic mechanical loss in millivolts at f = 14 Hz, heating rate 5 K min.$^{-1}$. A similar curve was found on cooling (7).

Table I. DSC Results on Linear Alkanes

Specimen a)	Exotherm b) Peak Temp.(K)	Start of Exotherm(K) 1st Heat b)	Start of Exotherm(K) 2nd Heat c)	Tu (K) d)
C_{30}	448	429	420	434
C_{36}	460	436	e)	435
C_{40}	460	440	423	453

a) Sample weights ranged from 1-3 mg.
b) Hermetically sealed pans.
c) Open pan for first heating, cooled to room temp., hermetically sealed, then second heating.
d) Open pan, first heating, sample weights ranged from 10-15 mg, from Ref. (3).
e) Sample not tested.

An early DSC run on PEO in 1981 revealed an exothermic peak when run in a hermetically sealed pan (MW = 5,000, 14.08 mg, 10 K min.$^{-1}$, 0.1 mJ s^{-1} cm^{-1}). The strong exotherm started at 395 K, and peaked at 425 K. Tu for this specimen (open pan) has been reported at 405 K (3). Figure 2 shows a more recent DSC trace of the same material (hermetically sealed) illustrating the strong exothermic peak starting around 405 K and peaking around 420 K. Cooling a specimen to 295 K and reheating shows only an endothermic slope change (Tu) at around 425 K.

A few preliminary DSC runs on Poly(4-methyl pentene-1) in hermetically sealed pans also show exothermic peaks, starting around 570 K and peaking at around 585 K. The top thermogram in Figure 3 shows such a peak for a first heating DSC run. It is difficult to avoid the conclusion that some connection exists between the exothermic peaks observed when using sealed pans and the Tu's observed with open pans.

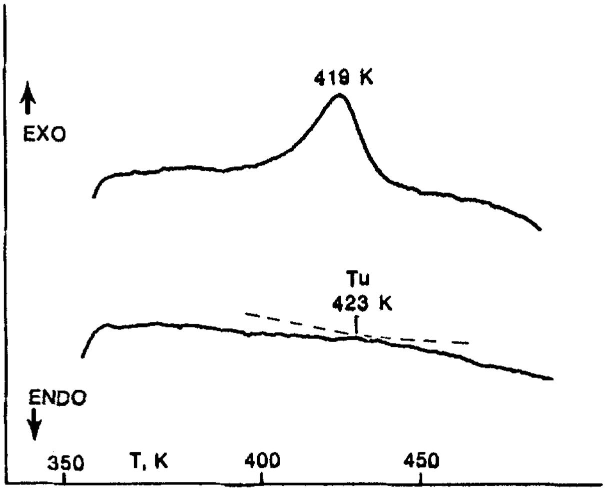

Figure 2. First (top) and second (bottom) heating runs on Poly(ethylene oxide), MW = 5,000, 12.88 mg, 10 K min.$^{-1}$, 0.1 mJ s^{-1} cm^{-1}, hermetically sealed pan.

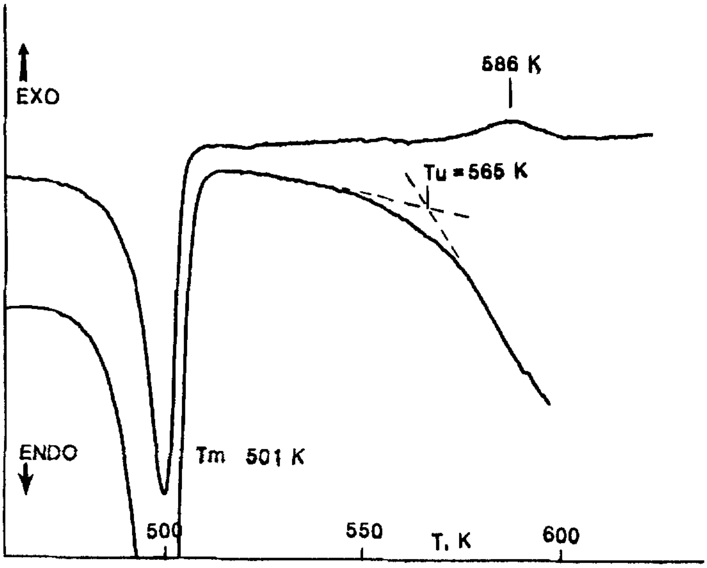

Figure 3. First heating DSC traces of Poly(4-methyl pentene-1), 10 K min.$^{-1}$, 0.1 mJ s^{-1} cm^{-1}, top-2.18 mg, hermetically sealed pan, bottom-6.70 mg, open sample pan.

Received and accepted January 24, 1983