

Effect of Scanning Speed of DSC on Determination of Melting Points of Crosslinked Polymers

This short note intends to add some more emphasis on the effect of DSC scanning speed on the experimental results.^{1,2}

Ahad,¹ for example, recently reported data on the melting points and heats of mixing of crosslinked PVA hydrogels. The crosslinking agents were chromium nitrate and/or potassium pyroantimoniate and the thermograms were obtained with a fixed scanning speed of 10°C/min. It is evident that change of the speed will shift the exotherms and eventually falsify the results. The following tests exemplify the effect of scanning speed and crosslinking density on the melting points of crosslinked samples.

Crosslinking was achieved by electron beam irradiation of degassed aqueous PVA solutions according to Bray's experimental procedure.³ The PVA used was Elvanol 73125 G of du Pont de Nemours with $\bar{M}_n = 88,800$ and $T_m = 222^\circ\text{C}$. The produced hydrogels were dehydrated at $25 \pm 1^\circ\text{C}$ and R.H. 40% for 90 days until constant weight (99.1–99.4% removal of water). Thermal analysis of the samples was done using DSC with scanning rate between 3° and 80°C/min. For normalization, experiments on dry uncrosslinked PVA samples were performed.

Table I shows that the melting points of dry crosslinked samples, calculated as the initial onset point of a DSC exotherm, depend on the scanning speed and the crosslinking density, as judged by the average molecular weight between crosslinks M_c .

For a typical sample, no. 202, a change of speed from 3° to 80°C/min shifted the melting point by 23°C. These data are in accordance with previous work on the melting points of crosslinked polymers⁴ and with Mandelkern's theory, which predicts that a higher crosslinking density (lower M_c), causes higher melting point depression.

The experimental work was partially performed at the Organic Chemical Technology Laboratories of the National Technical University of Athens, Greece.

TABLE I
Effect of Scanning Speed and M_c on T_m

Sample no.	Crosslinking density M_c	Scanning speed, °C/min	Melting point T_m , °C
201	uncrosslinked	3	221
		5	218.5
		10	216.5
		20	201
		40	194
		80	192
202	8420	3	215
		5	213
		10	211
		20	198
		40	192
		80	192
203	5715	3	207.5
		5	205.5
		10	204
		20	193
204	2190	40	189
		3	203
		5	201
		10	200
		20	190.5
		40	187.5

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