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were measured by means of differential scanning calorimetry (DSC) in order to study the nature of these relaxations with respect to the melting process of PEG.

PEG is a highly crystalline polymer. The calorimetric value  $\Delta H_m^a$  is related to  $\Delta H_m^c$ , the heat of fusion for 100% crystalline PEG, by  $\Delta H_m^c = \Delta H_m^a/a$ , where  $a$  is the degree of crystallinity of the sample.

The molecular weights ( $\bar{M}_n$ ) and the heats of fusion ( $\Delta H_m^a$ ) for PEG samples are given in Table 1. The crystallinities of

Table 1. Molecular weights ( $\bar{M}_n$ ) and the heats of fusion ( $\Delta H_m^a$ ) for PEG samples containing free (A) and covalently bound (B) nitroxyl radicals.

$\bar{M}_n$	A		B	
		$\Delta H_m^a$ (cal/g)		$\Delta H_m^a$ (cal/g)
1 000 ± 50		42.1		42.4
1 550 ± 100		45.1		46.5
2 050 ± 150		45.9		48.6
3 000 ± 300		49.4		47.7
4 000 ± 500		51.0		49.8
6 700 ± 700		50.1		49.4
9 500 ± 500		50.4		49.8
15 000 ± 2 000		48.2		49.3
22 000		49.4		46.8

## Studies on the Melting Process of Polyethylene Glycol

P. TÖRMÄLÄ and A. SAVOLAINEN

*Department of Wood and Polymer Chemistry, University of Helsinki, Helsinki, Finland*

Polymer samples containing minute amounts of free and covalently bound nitroxyl radicals were prepared in a study of the dynamic properties of polyethylene glycol (PEG).<sup>1</sup> The concentration ratio of radicals to polymer repeat units was very low (1 : 20 000). It was assumed that the radicals did not affect the bulk properties of polymer (*cf.* Ref. 2). Four different rotational relaxation regions were found in these samples. Melting region thermograms of PEG in the  $\bar{M}_n$  range 1 000–22 000

the samples (calculated by means of the  $\Delta H_m^c = 51.5$  cal/g of Beaumont<sup>3</sup>) are given in Fig. 1. The melting points ( $T_m$ ) of the samples are also shown in this figure.

From Fig. 1 is seen that the  $T_m$  of PEG increases rapidly until  $\bar{M}_n$  3000–4000 and thereafter slowly approaches its limiting value. These results are in accord with other measurements.<sup>3–6</sup> Evidently the differences between the  $T_m$  values of polymers containing spin probes and spin labels are caused by differences in the history of the polymers.

In the low  $\bar{M}_n$  region the degree of crystallinity is directly comparable to  $\bar{M}_n$ , while at high  $\bar{M}_n$  the crystallinities are lower than in the 4000–10 000 region. The decrease in crystallinity at high molecular weight is probably due to the increasing difficulty of a polymer molecule forming a crystal lattice.

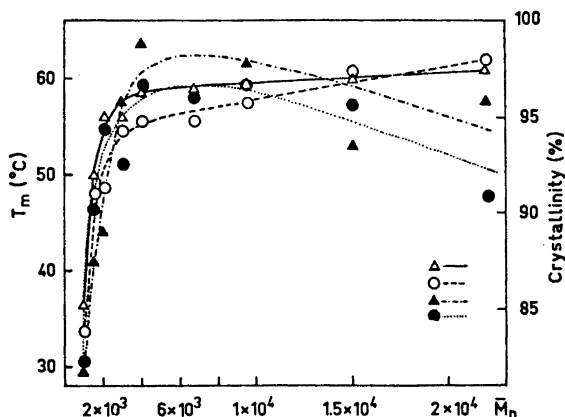


Fig. 1.  $T_m$  values and crystallinities of PEG samples as a function of  $\bar{M}_n$ ; symbols  $\Delta$  and  $\circ$  express  $T_m$  values of PEG containing free and bound radicals,  $\blacktriangle$  and  $\bullet$  are the crystallinities of the corresponding samples.

The melting of the polymer is located in the same temperature region where a strong change in the rotational relaxation times ( $\tau$ ) (sec) of nitroxyl radicals in PEG

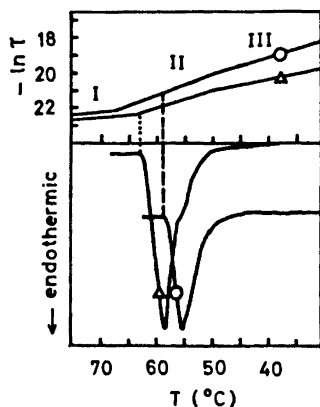


Fig. 2. DSC curves of PEG 4000 containing free  $\Delta$  and bound  $\circ$  radicals and their corresponding rotational relaxation Arrhenius plots.

was observed.<sup>1</sup> This can be seen from Fig. 2 where the DSC curves of PEG 4000 A and B and  $-\ln \tau$  values of spin probe and spin label radicals in these polymers are given as a function of  $T$ . When  $\bar{M}_n$

was  $\geq 1000$ , a similar correspondence between DSC and  $\tau$  measurements was also observed in other PEG samples.

It can be seen that the activation energy  $E_a$  of radicals in PEG reaches its maximum value in the temperature region (relaxation region II) corresponding to the endothermic melting process. Because segmental relaxations of surrounding polymer molecules contribute strongly to the  $\tau$  of radicals,  $E_a^{II}$  shows a strong change in short range segmental motions in the transition region II.

The endothermic DSC curve of PEG with free radicals correlates well with the corresponding  $E_a^{II}$  curve. The DSC curve of PEG 4000 B, however, does not correlate exactly with its relaxation II. Although PEG 4000 B melts at a lower temperature than 4000 A according to DSC, the transition temperature from relaxation region II to I in the former is clearly higher than the initial temperature of the endothermic change. This indicates that after the melting of the polymer crystals the environment of bound radicals is not yet liquid-like. The transition to a purely liquid-like state in the micro-environment of bound radicals occurs only some degrees above the end-point of the endothermic change. Because this phenomenon is not so prominent in the case of free radicals, it can be assumed that the effect is essentially intramolecular in origin. It is known that crystalline PEG in the solid state has

a helical conformation.<sup>7</sup> Since the esterified radical is in intimate contact with the host polymer, the transition from helix to a random coil conformation is a reasonable explanation for the observed phenomenon. It is thus probable that the polymer molecules in the relaxation region I are in a random coil conformation. Even if the helical conformations still exist, their fluctuations are so rapid that they do not affect the spin rotational relaxation.

Because the nitroxyl radicals incorporated into PEG exhibit a transitional relaxation region (II) in the temperature range where the endothermic melting of polymer crystals occurs, it is evident that radicals are in close contact with the crystalline phase. The isotropic nature of the ESR spectra refers to the amorphous environment.<sup>1</sup> On the other hand, the bulky radicals would surely distort the tightly packed crystal lattice about them and exhibit an amorphous-like environment even though they were in the crystalline phase. The structural changes in the crystal phase are thus reflected in the rotating radicals as changes in the forces caused by crystalline phase in the amorphous environment of radicals. This hypothesis is supported by the observation that in the  $\bar{M}_n$  region, where end group effects become negligible ( $\bar{M}_n \geq 9500$ ), the degree of crystallinity and  $E_a^{\text{II}}$  decrease as a function of  $\bar{M}_n$  (Fig. 1 in this report and Fig. 6 in Ref. 1).

*Experimental.* The PEG samples were of commercial origin (Fluka and Merck). Their  $M_n$  values were measured by a vapour pressure osmometer (Perkin-Elmer Modell 115) in chloroform at 32°C. The spin probe radical 3-methoxycarbonyl-2,2,5,5-tetramethyl-pyrroline-1-oxyl and the spin label radical 3-PEG-carbonyl-2,2,5,5-tetramethylpyrroline-1-oxyl were prepared and incorporated into PEG as reported earlier.<sup>1</sup> The history of the polymers was as follows: The PEG samples containing spin probes (set A) were dissolved in chloroform and the solvent was carefully evaporated in vacuum. The PEG samples containing spin labels (set B) were dissolved in chloroform precipitated with ether and dried in vacuum.<sup>1</sup> All these procedures were carried out at room temperature (24°C). DSC-curves were scanned at a rate of 8°C/min in an N<sub>2</sub>-atmosphere using a Perkin Elmer DSC-1B calorimeter.  $T_m$  was measured from the maximum of the endothermic peak height.

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## Isolation of D-Galactaric Acid and Isocitric Acid from *Ferocactus acanthodes* Br. et R.

RANDI KRINGSTAD and  
ARNOLD NORDAL

*Institute of Pharmacy, Department of Pharmacognosy, University of Oslo, Oslo 3, Norway*

Phytochemical investigations during recent years have revealed that the predominating acids of several succulent plants are hydroxy acids, which are able to form lactones.<sup>1-4</sup> Some of these acids, like phorbic acid, were first isolated from a succulent.<sup>5</sup> The cumulation of hydroxy acids in succulent plants is undoubtedly connected with the unique form of metabolism that is so characteristic for this group of plants, and it is believed that