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CRYSTALLIZATION OF SYSTEMS OF WATER AND POLYOXYETHYLENE

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The thermal behaviour of systems of water and polyoxyethylenes (POE) of different molecular weights was investigated by differential scanning calorimetry at a cooling rate of 5 deg/min^{-1}. In the narrow concentration range 55–60 wt% POE, the systems showed a reduced crystallization ability or no crystallization at all. The tendency to supercooling in the water/POE systems is highest at eutectic and slightly higher POE concentrations, and rises with increasing POE molecular weight.

Results obtained by differential scanning calorimetry (DSC) on the behaviour during heating of mixtures of water and POE with different molecular weights have been reported previously [1]. It was shown that these systes form eutectic mixtures which melt at constant temperatures not dependent on the composition. They also show a supercooling tendency. Mixtures containing about 60 wt% POE display no endothermic peaks on heating, suggesting the lack of a crystal phase. It was assumed that stable complexes of water and POE are formed.

The subject of this study was the thermal behaviour of the same two-component systems on cooling. Similar results are not available in the literature.

Experimental

Three samples of POE were used: two low molecular weight POE samples, POE-1 and POE-2 (Merck), of average molecular weight $M_n = 1000$ and $M_n = 2000$, respectively and a high molecular weight POE-3, obtained in the Central Laboratory of Polymers of the Bulgarian Academy of Sciences, Sofia,

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showing $[\eta] = 6.08$ cm^3/g in benzene at 25° (average molecular weight $M_\eta = 1.8 \cdot 10^6$). Water was demineralized by double distillation.

The calorimetric studies were carried out in the range from 110 to $-90°$ on a DSC–111 differential scanning calorimeter (Setaram, Lyon) at a cooling rate of 5 deg/min^{-1}. Mixtures of water and POE were sealed in steel capsules and then heated at the same rate. The DSC results on the subsequent cooling were recorded, the reproducibility being satisfactory. The characteristic crystallization temperatures read from the DSC curves are the initial and final temperatures (T_c^1 and T_c^2, respectively), and the peak temperatures (T_c^{max}). T_c^1 and T_c^2 are the temperatures at which the peaks of the DSC curves deviate from the baseline.

The change in the crystallization enthalpy, ΔH_c, was estimated from the area of the crystallization peak.

Results and discussion

Figures 1–3 show characteristic DSC crystallization curves of water/POE systems during cooling. Depending on the composition, one, two or no exothermic crystallization peaks are exhibited. Table 1 shows the concentration ranges of the three different types of DSC curves.

Table 1

No.	Type of DSC curves on cooling*	Concentration of POE, weight fraction		
		POE–1	POE–2	POE–3
1	Curves with monomodal exothermic peaks	$0 \geqslant - <0.2$ $0.4 > - \leqslant 0.5$ $0.67 > - \leqslant 1.0$	$0 \geqslant - \leqslant 0.5$** $0.8 > - \leqslant 1.0$	$0 \geqslant - <0.1$ $0.4 \geqslant - \leqslant 0.47$** $0.7 \geqslant - \leqslant 1.0$
2	Curves with bimodal exothermic peaks	$0.2 \geqslant - \leqslant 0.4$	$0.6 > - \leqslant 0.8$	$0.1 \geqslant - <0.4$ $0.47 > - \leqslant 0.5$ $0.6 > - \leqslant 0.7$
3	Curves without exothermic peaks	$0.5 > - <0.67$ (0.54**)	$0.5 > - <0.6$ (0.57)	$0.5 > - <0.6$ (0.56)

* cooling rate 5 deg·min^{-1}
** eutectic concentration of POE

The results obtained allow the assumption that the high-temperature exothermic peaks are due to the crystallization of free water (*w* lower than 0.5) and POE (*w* higher than 0.5). Here, *w* is the weight fraction of polymer. The low-temperature exothermic peaks may be attributed to crystallization of the eutectic phases which were determined calorimetrically during heating [1].

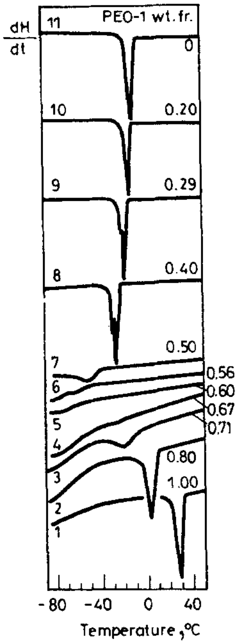

Fig. 1 DSC curves for water/POE-1 systems. Cooling rate 5 deg·min^{-1}

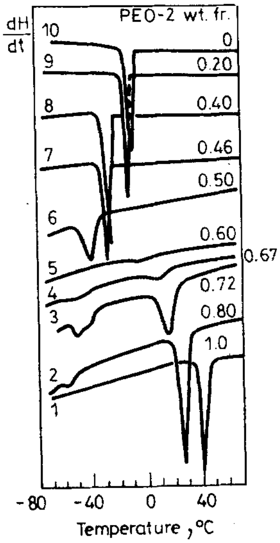

Fig. 2 DSC curves for water/POE-2 systems. Cooling rate 5 deg·min^{-1}

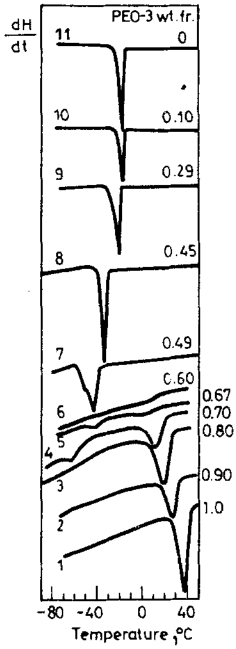

Fig. 3 DSC curves for water/POE-3 systems. Cooling rate 5 deg·min^{-1}

In the narrow concentration range 55–60 wt% POE, the systems showed a reduced crystallization ability or no crystallization at all.

With decreasing POE molecular weight, the concentration interval in which the water/POE systems do not crystallize during heating widens measurably. Further calorimetric studies showed that water/POE-1 systems ($w = 0.6$) do not crystallize even at a lower cooling rate (1 deg/min^{-1}), while water/POE-3 systems ($w = 0.6$) crystallize at −36°. The tendency to supercooling in these binary systems therefore increases with decreasing POE molecular weight.

Figures 4–6 present the characteristic crystallization temperatures of the systems as a function of their composition. Comparison with the phase diagrams drawn

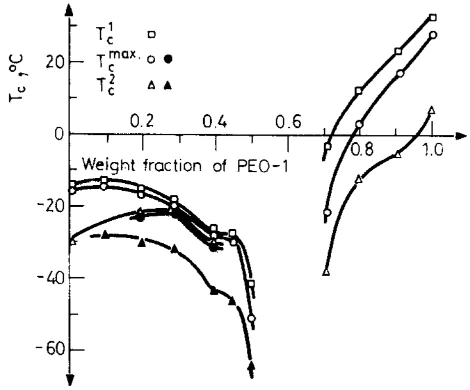

Fig. 4 Composition-dependence of the characteristic crystallization temperatures for water/POE-1 systems. Cooling rate 5 deg·min^{-1}. T_c^1 — (□); T_c^{max} — (○, ●); T_c^2 — (△, ▲)

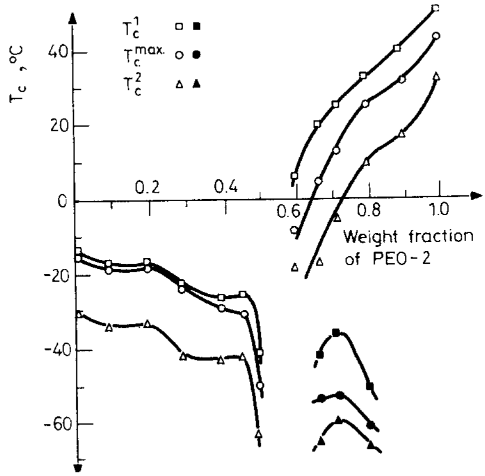

Fig. 5 Composition-dependence of the characteristic crystallization temperatures for water/POE-2 systems. Cooling rate 5 deg·min^{-1}. T_c^1 — (□, ■); T_c^{max} — (○, ●); T_c^2 — (△, ▲)

from the melting temperatures of the same systems [1] shows that they are similar except for certain specific differences. For example, for the systems which are heated and do not crystallize on cooling, there are no endothermic peaks in the DSC curves only in the case of the water/POE-1 systems (w = 0.6), while, as Figs 4–6 show, the curves for the composition-dependence of the crystallization temperature are interrupted for water/POE systems (w_{POE-1} = 0.5–0.7; w_{POE-2} = 0.5–0.6;

$w_{POE-3} = 0.56$–0.60). The solidus curves for the concentration-dependence of the characteristic temperatures T_c of the low-temperature exothermic peaks are seen in a narrow interval, and change as the liquidus curves do, probably because of the tendency to supercooling in the eutectic part of the system.

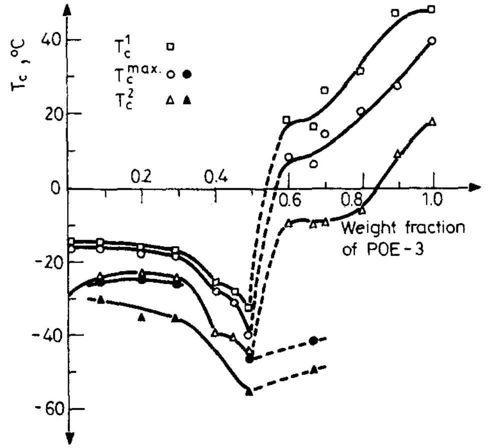

Fig. 6 Composition-dependence of the characteristic crystallization temperatures for water/POE–3 systems. Cooling rate 5 deg·min^{-1}. T_c^1 -- (□); $T_c^{\max}$ — (○, ●); T_c^2 — (△, ▲)

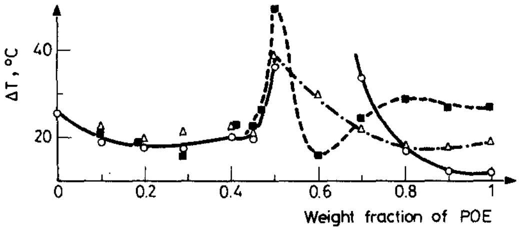

Fig. 7 Dependence of $\Delta T = T_m^{\max} - T_c^{\max}$ for free water and POE and for the eutectic phase on the system composition and polymer type: POE–1 (○); POE–2 (△); POE–3 (■)

Comparison of the melting and crystallization temperatures of free water, POE and the eutectic phase reveals that the difference $\Delta T = T_m^{\max} - T_c^{\max}$, which is a measure of the supercooling at the chosen cooling rate, is greatest at the eutectic and slightly higher POE concentrations (Fig. 7). On the whole, free water supercooling depends little on composition and POE molecular weight, while the supercooling of the eutectic mixtures and the free polymer increases with increasing molecular weight.

The increased tendency to supercooling in the eutectic systems may be explained by the formation of stable liquid water-POE complexes and the necessity for their components to be separated during their eutectic crystallization. It may be supposed that these complexes become more stable with increasing POE molecular weight.

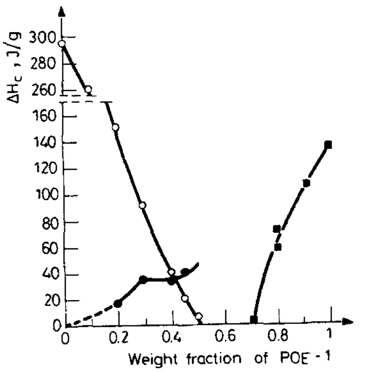

Fig. 8 Dependence of the enthalpy of melting of free water (○), POE (■), and the phase with the eutectic composition (●) on the composition of water/POE-1 systems

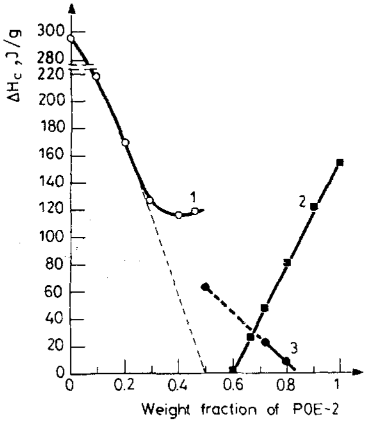

Fig. 9 Dependence of the enthalpy of melting of free water and the eutectic phase (curve 1), free POE (curve 2) and the eutectic phase (curve 3) on the composition of water/POE-2 systems

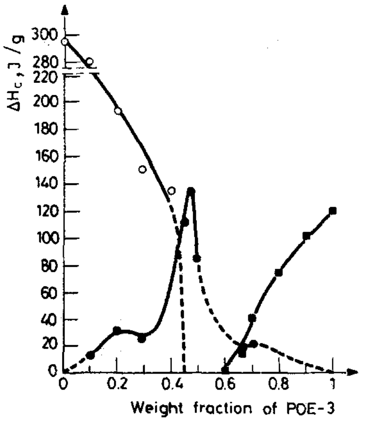

Fig. 10 Dependence of the enthalpy of melting of free water (○), POE (■), and the phase with the eutectic composition (●) on the composition of water/POE-3 systems

The composition-dependence of the crystallization enthalpy is presented in Figs 8–10. The crystallization enthalpies of free water and POE, measured in joules per gram of sample, decrease with decreasing w of the corresponding component, until their value reaches zero at $w = 0.5$ and 0.6–0.7 for POE–1 and POE–3, respectively. Since the crystallization exothermic peaks of the water/POE–2 systems are monomodal up to $w = 0.5$, curve 1 in Fig. 9 presents the composition-dependence of the sum of the crystallization enthalpies for free water and the eutectic phase. Extrapolation shows that the linear part of this curve intersects the abcissa at $w_{\mathrm{POE}-2} = 0.5$.

The maximum eutectic phase crystallization enthalpy is at the eutectic composition. On the other hand, the systems which do not crystallize, or crystallize only partially during cooling, do crystallize when heated above the glass-transition temperature [1]. Comparison of these results shows that the slopes of the curves for the composition-dependence of the crystallization enthalpy during heating coincide fairly well with the slopes of the curves for the concentration-dependence of the crystallization enthalpy during cooling, provided these crystallizations occur at the same time. Therefore, the supposition that the exothermic peaks exhibited during heating are due to the crystallization of the eutectic part of the systems is confirmed.

Reference

1 B. Bogdanov and M. Mihailov, Melting of systems of water and polyethylene oxide, J. Polym. Sci., Polym. Phys., 23 (1985) (in press).

Zusammenfassung — Das thermische Verhalten der Systeme von Wasser und Polyäthylenen (POE) verschiedenen Molekulargewichts wurde mittels DSC bei einer Abkühlgeschwindigkeit von 5° min^{-1} untersucht. In dem engen Konzentrationsbereich von 55–60 Gew.-% POE weisen die Systeme eine verminderte oder überhaupt keine Neigung zur Kristallisation auf. Die Tendenz der Wasser/POE-Systeme zur Unterkühlung ist bei eutektischen und etwas höheren POE-Konzentrationen am größten und wird mit ansteigendem POE-Molekulargewicht ausgeprägter.

Резюме — С помощью дифференциальной сканирующей калориметрии исследовано при скорости охлаждения 5°/мин поведение системы вода — полиоксиэтилен (ПОЭ) различного молекулярного веса. В узкой области концентраций ПОЭ (55–60 вес. %) системы обладают более слабой способностью к кристаллизации или же вообще не кристаллизуются. Тенденция системы вода — ПОЭ к переохлаждению достигает наивысшей степени при эвтектической или чуть более высоких концентрациях полиоксиэтилена и повышается с увеличением молекулярного веса ПОЭ.