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Study of Isothermal Crystallization of Poly (4-Methyle-1-Pentene) [P4MP] from Melt Using Differential Scanning Calorimetry

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Abstract: ***A systematic study of isothermal crystallization of P4MP from melt has been carried out using differential scanning calorimeter (DSC). The DSC curve from melting of the sample crystallized under different condition show two melting peaks (endotherms). This phenomenon has been investigated in detail and it has been shown that the one peak I is due to the melting of the isothermally crystallized fraction while the other melting peak namely peak II Is due to the melting of fraction which recrystallized or reorganized on heating.***

Keywords: Differential Scanning Calorimeter (DSC), Poly 4-Methyle-1-Pentene (P4MP)

1. Introduction

Poly **(**4-Methyle-1-Pentene) has very interesting scientific and technological properties.Poly (4-Methyle-1-Pentene) samples crystallized isothermally melt often show double melting endotherms. Appearance of such endotherms is intimately connected with the crystallization conditions and heating rate employed in DSC. Conflicting theories about the origin of this phenomenon have been put forward. It has been attributed to different crystal morphologies as well as partial melting and recrystallization. However no clear picture has yet emerged. To prove a better understanding of the isothermal crystallization process and the origin of multiple melting endotherms a systematic study of this process from melt has been carried out.

2. Experimental Detail

2.1 The P4MP sample used in the present study was obtained from British Petroleum Ltd. The number average molecular weight of the polymer used was 7 x 10^4 . The sample granules had a melting point 411K.

The isothermal crystallization and melting studies were carried by out using Perkin-Elmer differential scanning calorimeter model DSC-1B. The temperature scale of the instrument was calibrated using a standard reference material. The primary reference was Indium (T_m =429K). The melting temperature was determined from the location of the melting endotherms maximum. Whenever a material under goes a change in physical state, such as melting or translation from one crystalline form to another or whenever it reacts chemically, heat is either absorbed or librated. The DSC records the difference between the enthalpy change which occurs in a sample and that in some inert reference material, when both are heated under identical condition. It records the energy required to establish a zero temperature difference between a substance and a reference material against either temperature or time as the two specimens are subjected to identical temperature regime in an environment heated or cooled at a controlled rate.

2.2 In every case 5-7mg, of the sample was first heated upto 445K in the sample can of perkin Elemer DSC and kept at this temperature for about 20 min. This procedure was adopted to wipe out any previous morphological history of the sample. The sample was than rapidly cooled to the crystallization temperature T_c and kept at this temperature for a desired length of time. The crystallization was terminated by cooling the sample rapidly (>32K/min) to the room temperature. The DSC curves for melting of the isothermally crystallized sample were recorded at a rate of 8K/min. However to avoid any degradation of the polymer, crystallization or melting was always carried out in dry nitrogen atmosphere. To investigate the effect of heating rate sample crystallized under identical conditions were heated at different rate.

3. Results and Discussions

3.1 The DSC curves for melting of the isothermally crystallized samples of P4MP showed two peaks. The peak at low temperature has been called as the peak I while at higher temperature has been labeled as peak II. Some such typical DSC curves are shown in figure I. The set of curves as shown in figure I(a) represents the melting behaviour of samples crystallized at different temperature (Tc).The effect of heating rate at the sample crystallized at given temperature is

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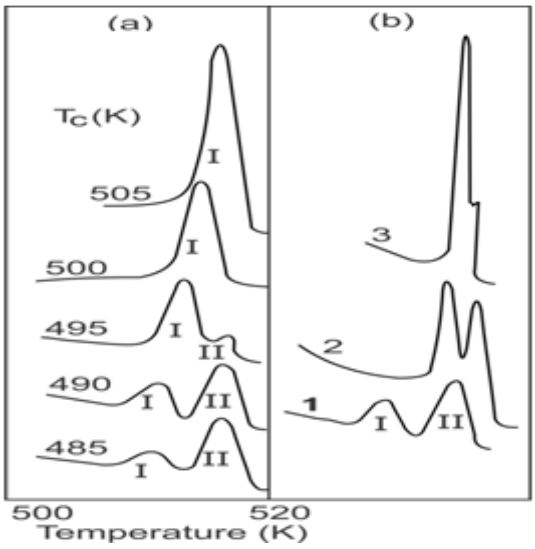

DSC fusion curves of the melt crystallized P4MP samples(a) effect of crystallization temperature(T_c) and (b) effect of heating rate for a sample crystallized at T_c=490K the curve 1,2 and 3 correspond to heating rate 4,8and 16K/min. shown in figure I(b).

3.2 Effect of Heating Rate

It is observed that on increasing heating rate the area under peak I increase at the expense of area under peak II. This effect is better representing in figure II where the areas under the two peaks are plotted as a function heating rate. It suggests that on melting some kind of re-crystallization takes place on the basis of these observations, it can be concluded that the peak I corresponds to the melting of the crystals formed during isothermal crystallization .

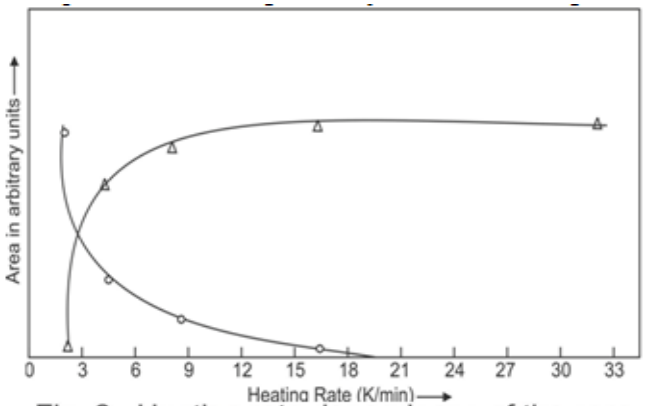

Fig. 2 : Heating rate dependence of the area under two peaks : Δ- Peak I and O - Peak II

At low heating rate the sample crystallized at lower temperature (Tc) can reorganized or re-crystallized to increase its stability and consequently melt at a higher temperature corresponds to peak II. The reorganization process involves either crystal perfection or crystal thickening. The former process take place at very low heating rate and involves solid transition at the phase boundaries yielding crystals which are of higher degree of perfection melting at higher temperature (Tm). Further, on increasing the heating rate less time is available for the crystal perfection to take place but on other hand some fraction of original crystallites can melt and re-crystallized at higher temperature leading to thicker and more perfect crystals. These crystals would also melt at higher temperature. As the heating rate increases, further the time available for reorganization or re-crystallization decreases and hence the friction of sample undergoing this process also decreases. As a consequence of this the area under peak I is expected to increase while area under peak II deceases with increasing heating rate. Thus, at fast enough heating rates only peak I is observed while at very slow heating rates only peak II is observed. These observed results are in agreement with these conclusions.

3.3 Effect of Crystallization Temperature

As shown in figure I(a) at a constant heating rate area under peak II decreases with an increase in crystallization temperature whereas area under peak I increases, further its melting temperature also increases. As crystallization temperature is raised the stability of crystals formed initially goes on increasing. As a consequence of this on increasing the crystallization temperature lesser and lesser fraction of isothermally crystallized part under-goes re-organization or re-crystallization on heating. Thus with increasing crystallization temperature at a given heating rate the area under peak I increases while that area under peak II decreases. At a Tc ≥ 500 K sample crystallized for sufficient length of time on melting only peak I is observed. It can there for be concluded that at Tc ≥ 500 K initial crystal formed during isothermal crystallization are stable, more perfect and thicker and hence the reorganization or re-crystallization process do not take place on heating , hence only one melting peak I is observed with higher melting temperature. This observation is an agreement with our conclusion.

4. Conclusion

On the basis of above mentioned observations it is concluded that, peak I is due to the melting of the isothermally crystallized fraction while the other melting peak II is due to the melting of the fraction which is re-crystallized or re-organized on heating.

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