Thermal Analysis of Polypropylene Grafted with Polyacrylic Acid*

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Melting points and heats of fusion of various polymers consisting of polypropylene grafted with polyacrylic acid, free from homopolymer and obtained under different conditions, have been examined. The melting point decreases on increasing the percentage of the initiator in the reaction of grafting, but is essentially independent of the amount of the grafted monomer at constant initiator/polypropylene ratio. This is related with the small density of branching, due to the grafting reaction which causes small variations of structure.

The existence of a two-phase system has been demonstrated by electron microscope.

The radical graft polymerization of several monomers on crystalline polymers often leads to the synthesis of compounds consisting of an amorphous and of a crystalline phase [1]. The influence of branching density on the physical properties of grafted polymer is still unknown, especially because it is difficult to measure such density. Properties undoubtedly are a function of the chemical nature of the two polymers, of the length and number of grafted chains. We thought it interesting to study the dependence of both melting points and heat of fusion of a crystalline polymer, either in the absence or in the presence of grafted chains, in order to clarify some aspects of this problem.

We have chosen polypropylene (PP) as crystalline polymer and polyacrylic acid (PAA) which is amorphous, as grafted polymer.

Experimental

Grafted polymers were prepared according to a method previously described [2]. It consisted in dissolving PP in o-dichlorobenzene (ODB) at 120°C, in adding a radical initiator (Bz₂O₂) and then acrylic acid (AA) under inert atmosphere. After the fixed time (a few hours) the polymeric product obtained was cooled, poured into acetone excess, filtered, subjected to boiling methanol extraction of the homopolymer and dried. The percent amount of grafting was determined by elemental analysis by an i.r. method.

already described [3]. The polypropylene samples used for comparison were dissolved at 120°C, for the same time in ODB or in ODB with the wanted percentage of Bz₂O₂, precipitated in acetone excess, filtered and dried.

Melting points and heats of fusion were determined by a DSC 1B Perkin—Elmer differential calorimeter, conveniently calibrated with indium standard. Samples of about 10 mg by weight were sealed in the proper aluminium sample pans and heated with a thermal excursion rate of 8°C/min. No preliminary heat treatment was made. Temperatures have been determined in repeated runs with the approximation of ±1°C, heats of fusion with the approximation of 0.5 cal g⁻¹.

Owing to the characteristics of the apparatus [4], heats of fusion were obtained by simple planimetric measurement of the area under the melting peak, whereas the final temperature of the endothermic peak was assumed as melting point. This last procedure proved to be the most satisfactory and reproducible, being the least sensitive to the unavoidable pre-melting phenomena.

Photographs were taken of grafted polymer samples, free from homopolymer, compression moulded between two aluminium sheets for 5 minutes, at about 170°C, and at a pressure of 50 kg cm⁻².

Transmission (Siemens Elmiskop IA) and scanning electron microscopes (Jeol JSM-U3) were used.

The two types of observation required different techniques for sample preparation: in the first case, the sample had previously undergone a 24-hour treatment, with a 2% aqueous solution of osmium tetraoxide and included in glycol methacrylate according to [6].

Observation by scanning electron microscope required only conductance of the cross section of the sample directly obtained by microtome cut. To this purpose, the cut surface was covered, by evaporation under vacuum, by a thin gold film (about 200 Å) and soon examined under the microscope.

The analysis of total peroxidic oxygen was carried out according to a known method [7, 8] consisting in suspending 1 g of substance in 50 ml of glacial acetic acid, in which nitrogen had been previously bubbled, then in adding freshly distilled hydroiodic acid at 57%. It was refluxed for 1 hour under inert atmosphere. After cooling, deaerated water (100 ml) was added and titrated with sodium thiosulfate 0.02N.

A parallel blank run was carried out under the same conditions, but in the absence of polymers. Active oxygen was calculated from the difference in thiosulfate consumption in the two cases.

**Results**

First of all we thought it convenient to study by differential thermal analysis the behaviour of PP alone treated by a procedure identical with that of the preparation of graft products, i.e. in the presence of Bz₂O₂ in ODB solution.

The results are listed in Table 1.

As may be seen, melting points (T_m) and heat of fusion (Q) decrease on increasing the Bz₂O₂/PP ratio; the molecular weights decrease. These findings suggest that Bz₂O₂ causes chain rupture and chemical changes that are proved by active oxygen analysis (Table 1). Gradient density column measurements we did (Table 1) show that on increasing the percent amount of peroxide, crystallinity does not change appreciably. Infrared analysis of the ratio between the bands at 974 and 995 cm⁻¹ [9] of the different samples
Table 1
Thermal properties, intrinsic viscosity, density and total oxygen content of PP sample treated in ODB solution at 120°C for 7 hours with different Bz$_2$O$_2$/PP ratios

<table>
<thead>
<tr>
<th>Parts of Bz$_2$O$_2$ over 100 parts of PP</th>
<th>$T_m$ [°C]</th>
<th>$Q$ [cal g$^{-1}$]</th>
<th>[$\eta$] tetralin 135°C (100 cm$^3$/g)</th>
<th>Density [g cm$^{-3}$]</th>
<th>Total oxygen content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>171</td>
<td>20.5</td>
<td>0.87</td>
<td>0.901</td>
<td>0.025</td>
</tr>
<tr>
<td>0.4</td>
<td>166</td>
<td>20.5</td>
<td>0.87</td>
<td>0.903</td>
<td>0.027</td>
</tr>
<tr>
<td>10</td>
<td>166</td>
<td>20</td>
<td>0.88</td>
<td>0.903</td>
<td>0.027</td>
</tr>
<tr>
<td>20</td>
<td>161</td>
<td>18.5</td>
<td>0.79</td>
<td>0.899</td>
<td>0.032</td>
</tr>
</tbody>
</table>

of Table 1, which is an index of tacticity which can be assumed, for equal thermal history, as an index of crystallinity, revealed to be of no practical aid for so small density deviations.

As known, crystallization is easier with lower molecular weights and therefore a higher $\eta$ should be observed; in our case molecular weights do not change very much, but are decreasing with increasing Bz$_2$O$_2$ percentage. We observed from experiments that $\eta$ and $T_m$ decrease. The reasons for such decreases are not clear, but could be attributed to a partial crosslinking and to the formation of peroxydic and hydroperoxide group; that may hinder chain regularity and hence crystallization.

We then examined the melting point and heat of fusion of different samples consisting of PAA grafted on PP with PAA contents varying from 0 to 57%. The different percentage of PAA was obtained by using the same amount of Bz$_2$O$_2$ (4% of PP), but different reaction times and monomer amount, the other conditions being the same.

Fig. 1 shows that melting point is practically independent of the PAA percentage. Obviously the heat of fusion of different samples is different, especially owing to the dilution effect. It is therefore important to refer heat of fusion of the grafted sample to their PP content only.

Fig. 1 shows the ratio between the heat of fusion of a PP gram ($Q_0$) in the grafted sample and the heat of fusion of a gram of PP homopolymer ($Q_{PP}$). As may be seen,

![Fig. 1. Melting point $T_m$ and $Q_0/Q_{PP}$ (heat of fusion $Q_0$ cal g$^{-1}$ PP of grafted samples/heat of fusion of PP) vs. PAA percentage at constant Bz$_2$O$_2$/PP ratio.](image-url)
such a ratio is practically independent of composition. This indicates that the two polymers, although chemically bound, behave as independent polymers without considerable interactions. This is proved also by the photographs taken by the electron microscope (Fig. 2), where the existence of distinct microphases is evident, and also by mechanical dynamical tests [1].

In order to evaluate the influence of the percentage of initiator on the thermal properties of the grafted polymers, we carried out some runs on polymers obtained with different percentages of $\text{Bz}_2\text{O}_2$, the other conditions being the same. It was thus found that melting point and heat of fusion for unit weight of PP are functions of the percentage of peroxide used.

Table 2 shows the melting points and heats of fusion for g of sample and for g of PP as the percent amount of $\text{Bz}_2\text{O}_2$. A comparison of these data with those obtained with PP treated with $\text{Bz}_2\text{O}_2$ without monomer is shown in Fig. 3. The percentages of grafted PP decrease on increasing the $\text{Bz}_2\text{O}_2$/PP ratio, in agreement with what previously stated [3,5]. Melting points and heats of fusion in cal g$^{-1}$ PP decrease on increasing the percentage of initiator used.

**Table 2**

Thermal properties of PP grafted with PAA, obtained in ODB solution at 120°C for 7 hours with a AA/PP ratio = 2 and with variable $\text{Bz}_2\text{O}_2$/PP ratios

<table>
<thead>
<tr>
<th>Parts of $\text{Bz}_2\text{O}_2$ over 100 parts of PP</th>
<th>Percentage of grafting</th>
<th>$T_m$ [°C]</th>
<th>$Q$ [cal g$^{-1}$]</th>
<th>$Q$ [cal g$^{-1}$ PP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>25.6</td>
<td>167</td>
<td>19.2</td>
<td>20.5</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
<td>165</td>
<td>14.6</td>
<td>18</td>
</tr>
<tr>
<td>15</td>
<td>19.1</td>
<td>162</td>
<td>14.9</td>
<td>18.5</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
<td>159</td>
<td>14.8</td>
<td>17.4</td>
</tr>
</tbody>
</table>
On decreasing the percentage of grafting, with increasing Bz$_2$O$_2$/PP, heat of fusion constancy in cal g$^{-1}$ PP is not observed, as might have been expected from the results of Fig. 1. This demonstrates that the structure of grafted polypropylenes is influenced by the Bz$_2$O$_2$/PP ratio.

![Graphs showing percentage of PAA, melting point $T_m$, and heat of fusion $Q$ vs. Bz$_2$O$_2$/PP ratio.](image)

*Fig. 3. Percentage of PAA, melting point $T_m$ and heat of fusion $Q$ (cal g$^{-1}$ PP) of grafted and ungrafted samples vs. Bz$_2$O$_2$/PP ratio.*

- ▲ grafted samples; ■ polypropylene.

Actually, Fig. 1 shows that the percentage of grafted product, the amount of initiator being the same, has not much importance for $Q$ and $T_m$. Fig. 3 concerning the grafted polymers shows that, on decreasing the percentage of grafting, $Q$ and $T_m$ decrease: this decrease must be ascribed to the increase of the Bz$_2$O$_2$ percentage used, the other conditions being the same.

The data of Fig. 3 show that percentage of initiator used during the reaction of grafting has some influence on $Q$ and $T_m$, the values of $T_m$ and $Q$ in cal g$^{-1}$ PP being lower than those observed in the case of PP treated with Bz$_2$O$_2$ without monomer.
Conclusions

Radical reactions of grafting give branched polymers. Owing to the difference in chemical nature of the two polymers constituting the grafted product, these, for thermodynamic reasons, tend to form distinct phases [10]. The percentage of grafted polymer being the same, two limit possibilities exist:

a) long and not frequent branches;
b) short and frequent branches.

Provided that grafted chains are sufficiently long, they tend to agglomerate in micro-phase independent of the one of the backbone polymers that, in our case, is crystalline. In case a) the crystalline polymer should keep almost unaltered from the morphological point of view, except in the regions near grafting.

In case b) a considerable hindrance to crystallization of the backbone polymer must be expected.

Hence, under the usual conditions of synthesis, the points of grafting are not frequent; therefore, the variations of the thermal properties of the grafted crystalline polymer with respect to those of the not grafted backbone cannot be very important.

The runs we carried out proved that (the amount of initiator used in the synthesis being the same) the thermal properties ($Q$ cal g$^{-1}$ PP and $T_m$) of the crystalline part in the grafted samples do not depend on the percentage of grafted amorphous phase. On the other hand, when using different amounts of initiator, until very high values of the $\text{Bz}_2\text{O}_2/\text{PP}$ ratio, which are unusual in the ordinary synthesis, we found a larger decrease of $Q$ and of $T_m$ than that observed by treating PP alone with the same percentage of initiator, in the absence of monomer. This suggests that the morphology of the system is shifted toward situation b).

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References