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ANALYSIS OF PHYSICAL AND CHEMICAL NETWORKS BY SLOW DSC AND TURBIDIMETRY

P. Bernazzani and G. Delmas

Chemistry Department, University of Quebec in Montreal, CP 8888 succ centre-ville,
Montreal, Canada H3C 3P8

Abstract

Semicrystalline polymers are made of a crystalline phase and of an amorphous phase. Recently, NMR, Raman and FTIR experiments have identified a third phase comprised of defects such as tie-molecules, in the organization of chains. Our investigation of physical gels has led us to believe that by following the heat flow in a very slow temperature ramp (0.05 K min^{-1}), phase-changes, unnoticed in the usual fast ramp, could be detected. These are associated to a physical network strained in the temperature ramp. In order to obtain more information on the network phase, the polymer has been crosslinked The characteristics obtained by slow calorimetry and turbidimetry of the original and modified materials are compared.

Keywords: DSC, network, polyethylene, turbidimetry

Introduction

Polymers are traditionally thought to be two-phase materials. A rigid crystalline phase and a liquid like amorphous phase. Recent papers on the morphology of polyethylene (PE) have investigated the possibility of the existence of a third semimobile phase [1, 2]. Although many hypotheses have been proposed to explain the existence of such a phase, they all seem to point to the presence of order in the amorphous phase. Further calorimetric (DSC) studies have noted the presence of a high temperature endotherm due to strain melting [3, 4]. As the temperature was increased at a very slow rate, the tension in polyethylene and polypropylene, increased. This increase suggests the presence of entanglements present mainly in the amorphous phase. The presence of entanglements in polymers has been widely accepted, their overall effect on thermal properties being usually neglected. However, the results from DSC in a slow temperature ramp show that these entanglements accounts for the presence of the third semimobile phase in polyethylene which we will now call the physical network phase.

In order to investigate the validity of the relation between entanglements and the third phase in polymers, we will apply the new technique of slow calorimetry (DSC in a slow temperature ramp) to crosslinked polymers. We will therefore attempt to quantify by calorimetry the network content of polyethylene.

Crosslinked PE has been used extensively in industrial applications. The strength increase and swelling abilities of these polymers have been the driving

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force of this industrial interest as a variation in the crosslinked content will have non-negligible effects on the physical properties of the polymer. It is therefore of interest to obtain an efficient quantification method of measuring the network fraction. However, few characterization studies of crosslinked PE are found in the literature, and the only quantitative methods of determining the crosslinked fraction involves indirect measurements. These methods consist mainly in the extraction of the non-crosslinked fraction followed by its analysis by varying techniques. The main drawback of these methods resides in the faith that one must have in the ability of the solvent to extract all of the loose chains contained in the polymer. In the ASTM method, the recommended time for allowing this soluble fraction to separate is 12 h in xylene. Some authors [5] have found that a minimum of 48 h was necessary to reproducibly accomplish this task, making the experimental time very large. The new techniques of slow calorimetry [3, 4] and turbidimetry [6, 7] seemed appropriate for the analysis of the chemical networks since they have been known to measure physical networks.

Variation in the enthalpy of the network disordering

Based on previous experimental data [3, 4], we developed the hypothesis that slow differential scanning calorimetry represents an ideal solution. A high temperature endotherm assigned to the disordering of the network can be found using this method.

Experimental

Materials

The samples are linear low density polyethylenes from DuPont D(7) and D(12) and long chain branched polyethylene from Union Carbide, U(18). The figure in parenthesis correspond to their methyl content per 1000 carbons and are indicative of the amount of branching in the samples. Their molecular weight is between 10^5 and 2×10^5 g mol^{-1}. The branched sample U(18) was chemically crosslinked by peroxide addition (U(18C)) while linear and branched DuPont samples were crosslinked using gamma irradiation and noted D(7C), D(12C). Both these types are designated by the term chemical network.

Range of temperature

Previous analysis in slow DSC showed the presence of an endotherm after the melt of the crystalline phase of PE [3, 4]. Consequently, we measured the enthalpy variations up to 100 K after the fusion temperature.

Apparatus

The C80 calorimeter from Setaram is a sensitive DSC capable of accommodating large size cells (8 cm^3). Quantitative enthalpy measurements can be obtained at heating rates of 0.1 K h^{-1} however, we have limited ourselves to 3 and 12 K h^{-1} ramps.

The turbidity at the lower critical solubility temperature (LCST) measurements were made following the method described in previous works [6], using hexane as the volatile solvent. In this technique the amount of polymer phase separated on a given temperature interval is obtained through the turbidity, h_i, developed during the phase change. The sum of h_i (Σh_i) values over the complete interval of phase separation (typically 120 K), is proportional to the overall volume fraction of the polymer. For a crosslinked sample, only the polymer molecules extracted from the network contribute to the Σh_i. The ratio of Σh_i(crosslinked)/Σh_i(non-cross-linked) gives the fraction of soluble material. The amount of material that is nonsoluble is considered to be the network fraction. The ASTM method of quantifying the network fraction has also been followed.

Results and discussion

Variation in the melting enthalpy of the orthorhombic crystals

Table 1 shows the calorimetric data for both the untreated and crosslinked PE samples. The different columns show respectively the sample identification, the melt temperature (T_m), the enthalpy of fusion of the orthorhombic crystals, ΔH_{ortho}, the enthalpy of disordering of the network, ΔH_{net}, the total enthalpy, ΔH_{tot}, and the network fraction f_{net}. The figures in parenthesis below the values of ΔH_{net} give the temperature interval used for the integration of the network fraction. Shown in this table, their T_m and ΔH_{ortho} diminish as the samples are crosslinked, as found in the literature [8]. Column 3 shows the enthalpy variations of the orthorhombic fraction, ΔH_{ortho}. For all of the uncrosslinked polymers, we find that this value is around 170 J g^{-1} confirming the values found in the literature [9].

Crosslinked samples give a lower enthalpy variation and therefore contain about one half less orthorhombic fraction. This can be explained by comparing the formed network to the branching of a linear polymer. Impeded by these defects, the polymer will crystallize with more or less difficulty depending on the length of these branches, and reducing the overall crystallinity.

Table 1 Calorimetric data of varying crosslinked and non-crosslinked samples using a very slow temperature ramp

Polyethylene samples	T_m/°C	ΔH_{ortho}/J g^{-1}	ΔH_{net}/J g^{-1}	ΔH_{tot}/J g^{-1}	F_{net}/J g^{-1}
D(7)	130.4	184	66 (160–245)	250	0.25
D(7C)	129.8	152	142 (140–245)	294	0.49
D(12)	118.9	169	68 (160–250)	238	0.37
D(12C)	109.1	105	204 (150–250)	309	0.66
U(18)	112.8	147	53 (150–250)	200	0.27
U(18C)	107.7	108	217 (145–250)	325	0.66

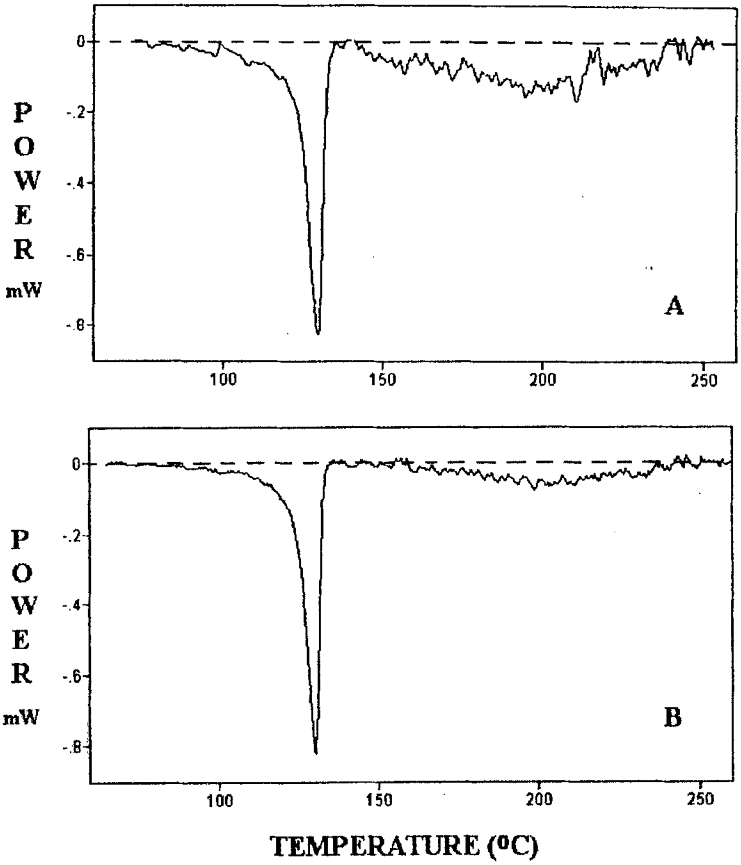

Fig. 1 Slow DSC traces comparing (A) D(7C) crosslinked and (B) D(7) unmodified samples. Both sample masses are equal

Figure 1A shows a typical calorimetric curve of irradiated D(7) from which the baseline was subtracted. The sharp endotherm corresponds to the melting of the orthorhombic fraction (T_m=130°C). The flatter endotherm at higher temperatures (160–245°C) is associated with the melt of the network. In this study, we have attributed this endotherm to the disordering of the region between the crosslinked chains. We therefore formulate the hypothesis that this new method can be used as a direct measurement of the crosslinked fraction in the samples.

The percentage of network fraction, f_{net} was calculated to be $(\Delta H_{net}/\Delta H_{tot})\times 100$ and is shown in column 6 of Table 1. From these values we note three points: a) the non-crosslinked samples have a small network fraction, b) the low density PE (LDPE) possess a higher content of network then the D(7), c) the chemically crosslinked polyethylene contains a higher network fraction than the irradiated samples. We will now explain further these points individually.

Uncrosslinked

The value of T_m reflects the amount of methyl content in PE's. A higher values of CH_3 corresponds to a greater amorphous content. The value of ΔH_{ortho} is seen to decrease with increasing branch content in D(7), D(12) and U(18) as expected [8]. ΔH_{net} of these uncrosslinked PE's have values between quarter and two thirds of the total enthalpy (ΔH_{tot}).

Figure 1b gives the trace of slow melting of the D(7) sample before irradiation. The similarity of both traces is clear, the two curves differ only by the magnitude of ΔH_{net}. The present work supports the identification of the high temperature endotherm associated in a previous work to a network. The network endotherm for the non-crosslinked samples is weak from the slow DSC traces. There is a reason for its presence: in irradiated samples, D(7) is compression moulded and quenched from the melt, which increases the chances of entanglements in the sample. At a certain point, the number of these entanglements is so great that a physical network appears. Further evidence of this was found when we observed a smaller high temperature endotherm in a D(7) sample that was slowly cooled. This physical network will be found in all polymers that contain entanglements but is usually neglected in phase composition measurements.

Chemically crosslinked samples

The value of T_m and ΔH_{ortho} is seen to diminish as predicted by the thermodynamics of copolymers [8]. The lowering of T_m and ΔH_{ortho} is larger for the more amorphous polymer D(12), which experienced the same irradiation dose as D(7). ΔH_{net} increases in D(7), D(12) and D(18) after crosslinking are 76, 136 and 160 J g^{-1} respectively. Crosslinking has the effect of increasing the amount of meltable network content as expected. The larger increase for D(12) compared to D(7) has the same origin as suggested above. The temperature interval on which the network fraction melt depend on the size of ΔH_{net} but apparently not on the value of the limits (physical or chemical). The high temperature endotherm has been explained as a consequence of strain melting. Expansion during the temperature ramp and also at T_m lead to strain in the melt crystals. Strain can be sufficient to stop the melting which resumes at high temperature. The hindering of mobility which lead to strain must not be very different in origin, if the hindrance is an entanglement or a crosslink.

Chemically crosslinked PE has a higher network fraction than all other polymers studied. This can be attributed to the fact that this sample is a low density slightly branched polymer as can be demonstrated by the low molecular weight. However, we believe that the main reason for this high fraction is the crosslinking method. The network content in a polymer has been linearly related to the amount of peroxide added. This method can therefore produce very high levels of crosslinks. It should be noted that a certain peroxide content was found after the chemical treatment is over which had to be removed by successive washes.

Comparison of network fraction

In order to confirm the quantitative nature of the calorimetric results, network fraction was obtained by two other methods: 1) The ASTM method of measuring

Table 2 Comparison of the fraction of network phase in different samples as measured by three methods, ASTM (in xylene), LCST (in *n*-hexane) and DSC (slow)

Polyethylene samples	F_{net} ASTM	F_{net} LCST	F_{net} DSC
D(7)		0.22	0.25
D(7C)	0.65	0.54	0.49
D(12)		0.39	0.37
(D12C)		0.66	0.66
U(18)			0.27
U(18C)	0.75		0.66

the amount of product dissolved in xylene, and 2) by LCST measuring of the amount phase separating from a hexane solution. The results are compared with those of slow DSC in Table 2. This table shows that for both irradiated samples, a high network fraction is found (55% for D(7) and 65% for D(12)), which agrees well with the calorimetric data. In fact the small difference between the two techniques is comparable to the standard errors of both techniques. However, the values found using the ASTM method are significantly higher for all the analyzed samples. We surmise that this is due to the extraction time being too little (12 h) to fully extract all the non-entangled chains. We conclude that the new slow DSC method to characterize the network fraction in a polymer is more precise and advantageous in that manipulations are kept to a minimum.

Conclusion

In this study, our goals were twofold to validate the hypothesis that a third semi-rigid fraction in polyethylene was composed of a physical network caused by chain entanglements, and to demonstrate that DSC using a slow temperature ramp was capable of accurately quantifying the network fraction either physical or chemical in polyethylene.

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