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THERMAL STABILITY OF LINEAR POLYDICYCLOPENTADIENE

Doina Dimonie[1x], Dimonie Mihai[2], Stela Stoica[1], Adina Cimpoeru[1],
Abadie Marc[3]

[1] Chemical Researches Institute, "ICECHIM", Bucuresti,
Spl.Independentei, Nr.202, Sector 6, 77208, ROMANIA
[2] ''Politehnica "University Bucuresti, Polizu 1, ROMANIA
[3] Université Montpellier II, Sciences et Techniques du Languedoc,
Laboratoire d'Etude des Matériaux Polymères, Matériaux Avancés
Organiques, FRANCE

SUMMARY : Thermal stability of linear polydicyclopentadiene (L-PDCPD) obtained with special binary catalytic complexes based on tungsten chlorides and allylsilanes derivatives is presented. It is shown that in the temperature range of 30-1000 ^{0}C, the principal thermal behavior of L-PDCPD, obtained with the above mentioned catalytic systems, consists of an endothermal transition that corresponds to the glass transition temperature and two other exothermal transitions corresponding respectively to thermal polymerization and thermo-oxidation.Thermal stability of L-PDCPD, thus a cyclic-based polyolefin with high degree of unsaturation all along the macromolecular chain, seems to be better than that of linear polyethylene chains, polymers known to be slightly branched. Thermal stability of L-PDCPD could likely be enhanced by a better control of the catalyst residues, and/or a proper stabilization, and/or an appropriate thermal treatment. Fast electron irradiation and temperature have different effect on L-PDCPD .

INTRODUCTION

The ring opening polymerization of dicyclopentadiene (DCPD) by opening of cyclopentene and norbornene rings with formation of a three dimensional polymer structure is well known [1,2].

The cross-linked polymer is marked for many years in USA (by Hercules and other companies) as a polymer with remarkable physical and mechanical properties, that can be molded by Reaction Injection Moulding (RIM) [3,4].

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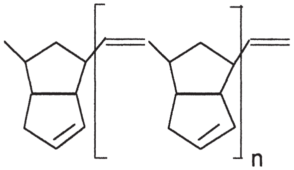
The ring opening polymerization of DCPD, with the opening only of the norbornene ring and the formation of a linear polymer (L-PDCPD – Scheme 1), is comparatively less studied [5-8].



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Recent studies show that for L-PDCPD synthesis special binary complexes based on tungsten chlorides and allylsilanes are very efficient catalytic systems.The resulted polymers have interesting and useful properties. They display high solubility in many organic solvents. By evaporating a L-PDCPD solution, elastic and resistant films with good adhesion properties on several substrates (wood, metal, glass, plastic materials) can be obtained. Also the polymers exhibit high resistivity and particular insulating properties [9].

Thermal stability of linear polydicyclopentadiene (L-PDCPD) obtained with the above mentioned catalytic systems is presented .

EXPERIMENTS

The thermal stability of L-PDCPD obtained by ring opening polymerization of DCPD with $WOCl_4$ and dimethyldiallylsilane has been studied. The stability has been measured on 0,01 mm thick L-PDCPD films (obtained from 15-20% toluene solution) by using the following methods:

- DSC, on a DuPont thermoanalyzer, in 30-450 ^{0}C temperature range with a heating rate of 10 °C/min.;

- DTA and ATG under air atmosphere, on a Q-1500 D Derivatograph, in 30-1000 ^{0}C temperature range.

The first exothermal peak was studied on 0,02 mm thick L-PDCPD films, obtained from 10% toluene solution, either untreated and previously treated by fast electron beams and temperature. Untreated and treated L-PDCPD films were characterized by DSC, on a DuPont thermoanalyzer, in the temperature range of 10-350 ^{0}C and a heating rate of 10 ^{0}C/min.

Irradiation was performed in an accelerator with fast electrons beams (1.8 MeV) at 6 mA and 3.5; 7; 10.5 and 14 Mrad irradiation doses.

The heat treatment was made under dynamic conditions in a DSC cell, by two heating cycles, first up to the end of the studied exothermal process and then, after sample cooling down, heating up to the oxidation temperature. The heating rate was 10^{0}C/min. The thermal treatment was done on a DuPont 2100 thermoanalyzer.

RESULTS AND DISCUSSIONS

PRINCIPAL THERMAL PROCESSES OF L-PDCPD

It has been observed that the DTA curves of all L-PDCPDs obtained with binary complexes based on tungsten chlorides and allylsilanes have the same shape. In all cases, an endothermal transition and two exothermal ones can be observed. The temperatures at which these thermal processes take place depend, in a certain extent, upon the catalyst-cocatalyst combination, their ratio and reaction conditions.

The obtained results are discussed here for L-PDCPD that was synthesized with $WOCl_4$ and dimethyldiallylsilane, that is totally soluble in toluene, and is characterized by a polydispersity index of 1,9. The assessment of the thermal behavior of the studied L-PDCPD has been done by simultaneous of DTA(fig.1), DSC(fig.2) and ATG (figs.1,3) analyses.

From DTA curve it can be observed that the principal thermal transitions of L-PDCPD are located at 40 °C, 200 - 370 °C range, and above 490 ^{0}C .

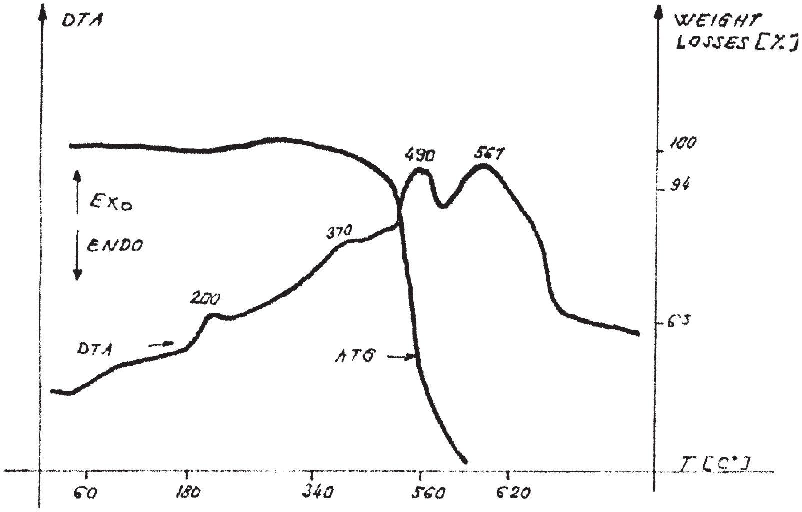

Fig. 1 : DTA-ATG curve of studied L-PDCPD (air).

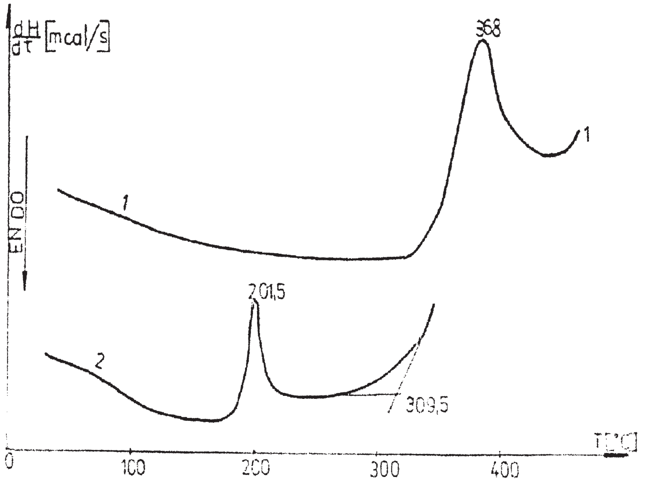

Fig. 2 : DSC curve of studied L-PDCPD under (1) argon and (2) air.

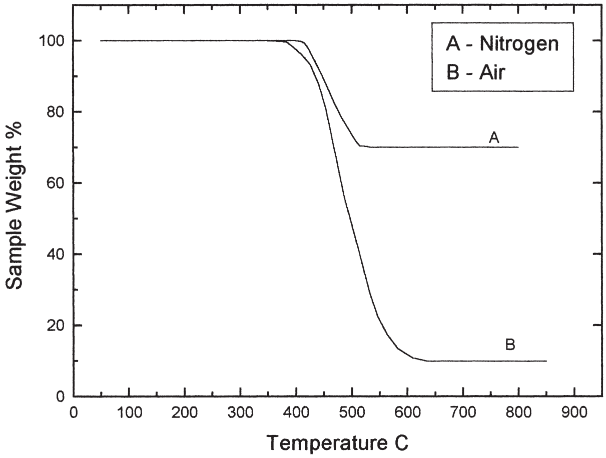

Fig. 3 : The weight losses versus temperature for studied L-PDCPD under (A) nitrogen and (B) air.

The endothermal second order transition around 40^0 C is *a glass transition* [9,10].

The next thermal transition takes place in air at ca. 200 ^{0}C (201,5 ^{0}C on DSC curve) and at 368 ^{0}C in argon atmosphere, respectively (fig.2). ATG curve shows that the polymer does not loose weight below 400 °C (ATG curves, fig. 1and 3), meaning that this DSC exothermal peak could be associated to the *thermal polymerization* of carbon carbon double bonds spread all along the polymer backbone. The study of the nature of this process will be presented hereafter.

It is worth noting that in the temperature range corresponding to the occurrence of that thermal process and after them (from 200 to ca. 360 ^{0}C) the ATG curves show a small increase of the sample weights by increasing the temperature (fig.1). Clearly, in this temperature range, *early stage thermooxidation reactions* take place as well. This process more likely occurs simultaneously with the presupposed thermal polymerization.

Furthermore, observations achieved on L-PDCDP by Boetius test indicate that a temperature increase above 200 ^{0}C triggers the yellowing of the polymer sample. At 350 ^{0}C, L-PDCPD gets brown and totally insoluble in toluene. This means that in this temperature range a degradation with cross-linking reactions takes place.

The thermooxidation become accelerated for L-PDCPD at 309,5 ^{0}C and have a maximum at 370 ^{0}C (fig.2). It is also observed that under argon atmosphere (fig.2) the first exothermal peak appears at a temperature at least 100 ^{0}C higher than when exposed in air. All these results make clear that, in air, the two exothermal processes, polymerization and thermooxidation respectively, occurs simultaneously.

The superposition, in air atmosphere, of presupposed thermal polymerization and thermooxidation in its very beginning stage might find explanation by the fact that thermooxidation products constitute initiators for double bonds polymerization.

The ATG curves (fig.1,3) show that L-PDCPD weight losses start at 360 and 500 ^{0}C in air and in nitrogen, respectively. To these temperatures correspond the time at which thermooxidation starts *to break down the macromolecular chains.* Above these temperatures the weight losses increase very much with the temperature increase. Up to 490 ^{0}C the weight losses are higher than 50%. At 650 ^{0}C the polymer is totally destroyed. Such a thermal behavior means that above this temperature values *the prevalent reaction in thermooxidation* is *the breaking of the L-PDCPD chains.*

In case the polymer has chain defects, like branchings, the beginning of weight losses is reported to occur in a much lower temperature range, even 300 ^{0}C lower [10].

Thermal stability of L-PDCPD, a cyclic-based polyolefin with a high degree of unsaturation all along the macromolecular chain seems to be higher than that of linear polyethylene, polymer that can be slightly branched (fig.4).

These results demonstrate that in the 30 - 1000 ^{0}C temperature range, the principal thermal behavior of L-PDCPD synthesized with catalyst combination based on tungsten complex and allylsilanes derivatives consists of an endothermal transition that corresponds to the glass transition followed by two other exothermal transitions. The first of them is probably associated to a thermal polymerization, whereas the second is a thermooxidation.

L-PDCPD is thus a polymer with a good thermal stability, probably better than that of LLD-PE. Note that its stability can probably be enhanced by a better catalyst residues control, or/and proper stabilization.

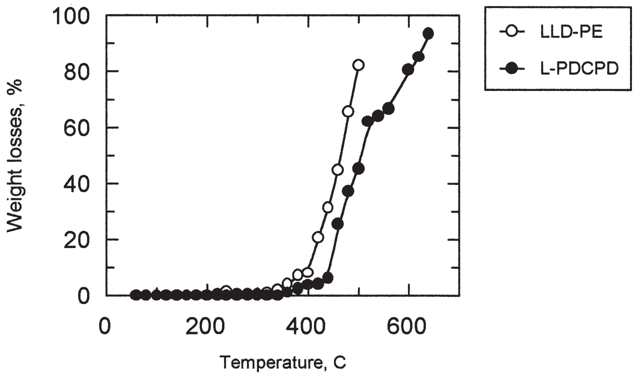

Fig.4 : Weight losses versus temperature for L-PDCPD and LLD-PE (air).

THE STUDY OF THE NATURE OF THE FIRST EXOTHERMAL PEAK ON DSC CURVE OF L-PDCPD

The temperature at the maximum of the first exothermal peak varies and depends on investigated catalytic systems and reaction conditions. For studying the nature of this peak, it was used a L-PDCPD for which the first DSC peak has a maximum at 149,9 ^{0}C and surface of 322,6 J/g (fig. 5).

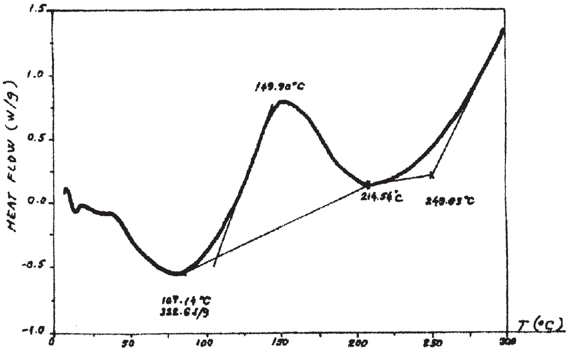

Fig.5 : First DSC exothermal peak of L-PDCPD (air).

It is observed at figure 6 that this peak does not disappear even for L-PDCPD chains previously electron irradiated (irradiation treatment according to the above described method) [11]. However, after a 2 h heating at 150°C, it was found that the studied peak fully disappears [11].

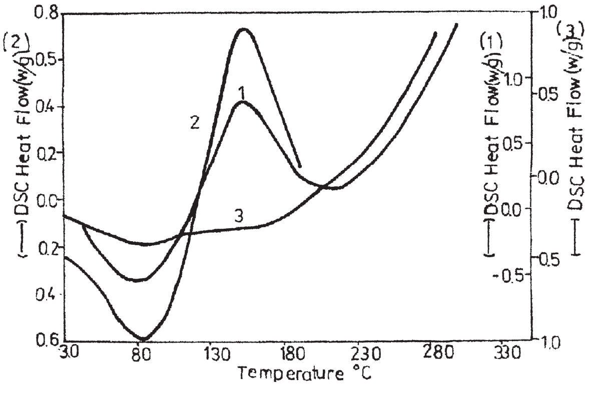

Fig.6 Thermal behavior of irradiated L-PDCPD : (1) untreated; (2) heat treatment and (3) after heat treatment (see text).

These results confirm that the exothermal peak at ca. 150 ^{0}C correspond to a *thermal polymerization,* and that this reaction, when carried out on this type of L-PDCPD, can be completed within 2 h at 150 ^{0}C. The FT-IR spectra of L-PDCPD before and after this thermal treatment, show, for treated polymer, an important change in the double bond range [11]. The FT-IR spectra of previously irradiated L-PDCPD do not show these changes before and after heat temperature, probably because at the moment of the thermal treatment the polymer is already cross-linked by irradiation The fast electron irradiation and temperature have different actions on L-PDCPD [11].

Preliminary works show that after an appropriate thermal treatment the L-PDCPD polymers have a new thermal behavior and a better thermal stability. One can also expect that such thermal treatments can enhance, to some extent, the thermal resistance of L-PDCPD.

CONCLUSIONS

1. In the temperature range of 30-1000 ^{0}C, the principal thermal behavior of L-PDCPD obtained with catalytic combination based on tungsten complex and allylsilanes derivatives consists of an endothermal transition that is a glass transition followed by two exothermal processes. The first of them represent a thermal polymerization and the second one is associated to a thermooxidation.

2. L-PDCPD, a cyclic-based polyolefin with a high degree of unsaturation along the macromolecular chain seems to be higher than that of linear polyethylene, polymer slightly branched. The ATG measurements show that the first weight losses begin at 350 ^{0}C and at 500 ^{0}C in air and in nitrogen, respectively.

3.Thermal stability of L-PDCPD can be probably enhanced by a better catalyst residues control, and/or a proper stabilization, and/or an appropriate heat treatment.

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