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Correlation between Temperature Setting and DCS Complex Peak Energy and in ROMP of Dicyclopentadiene

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Abstract

Polydicyclopentadiene is one of the most interesting advanced polymers. After ring open metathesis polymerization (ROMP) by using second generation Grubbs catalyst, we obtain a crosslinked polymer with good mechanical properties. Heating is used to initiate the polymerization process as well as to obtain a higher degree of crosslinking between the polymer chains. We try to analyze the correlation between second stage heating and the degree of cross-linking by using DSC-analysis. DSC analysis shows us a complex exothermic peak after glass transition temperature and this peak area was analyzed.

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1. Introduction

Dicyclopentadiene (DCPD) is one of the secondary products of petroleum processing. In normal conditions, it is solid with a specific odor and a melting point near 30-35°C¹. It has two double bonds – one in the norbornene cycle (strained and more active double bond) and a second one in the cyclopentene ring (less active double bond)^{2,3}. By using Grubbs metathesis catalyst, DCPD can react through ROMP (Ring Open Metathesis Polymerization) polymerization, after which we receive a hard and crosslinked polymer with good tensile (1700-1800 MPa) and bending (\approx 2000 MPa) modulus⁴. Poly-DCPD also has a very good chemical resistance and it can maintain its

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mechanical properties throughout a wide range of temperature (-60°C +160°C). We can see scheme of ROMP of DCPD on Figure 1:

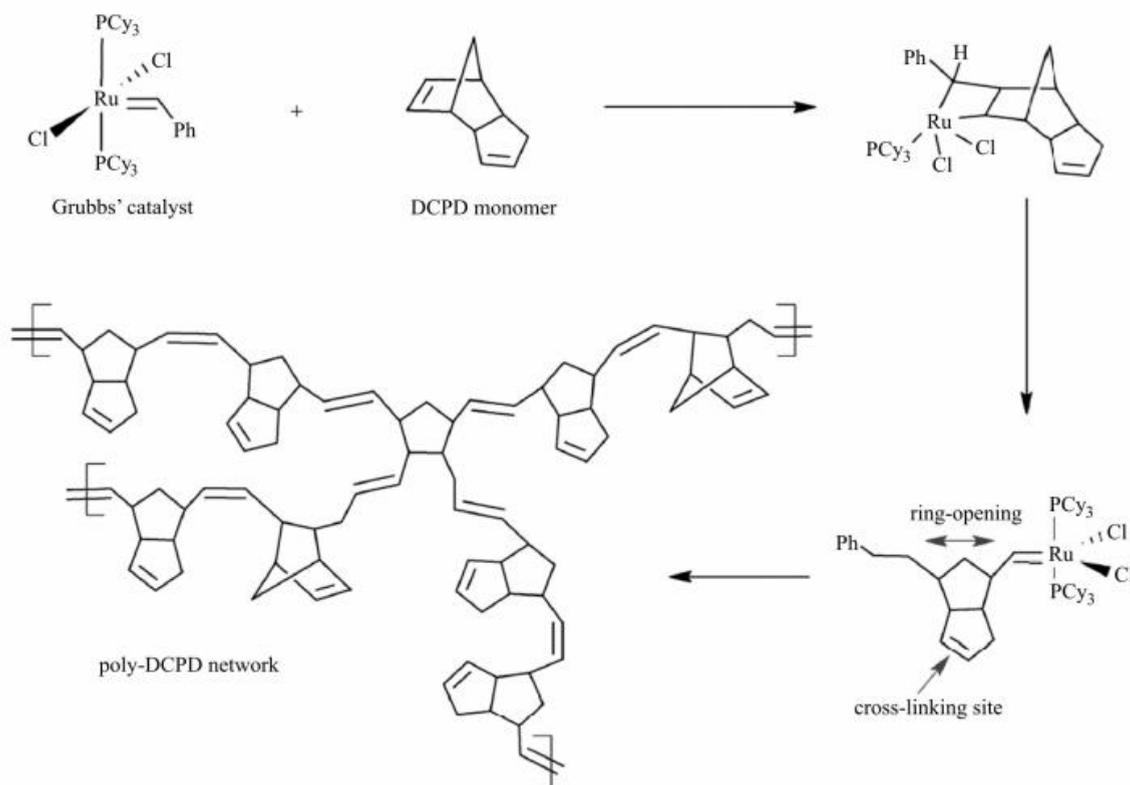


Fig. 1. Scheme of ROMP for DCPD by Grubbs catalyst⁵

It is believed that Grubbs catalyst initiates the opening of the norbornene ring because this ring is more strained and more reactive. After the double bond in the norbornene ring is opened, a lot of energy is produced and a self-heating process is started (self-sustaining exothermic reaction)^{6,7}. The temperature of this self-heating can be very high (near 180°C) and this energy starts the second stage of polymerization – producing cross-linking and opening cyclopentene ring. However, this energy may not be enough to obtain a good cross-linked polymer and in industry or lab conditions some additional heating is used. After this heating, the glass transition temperature (usually this temperature shows the degree of cross-linking) rises and the complex peak on the DSC curves decreases or totally disappears. A second DSC analysis of the same sample is done to verify that there is no more peak and no other thermal effects are present.

2. Materials and Methods

To generate experimental data we used purified DCPD (99.8% purity) with 6-8% tri-DCPD. For the purification, sodium was added to the DCPD and boiled under low vacuum (50 torr) using a rotary evaporator. All operations and storage of the prepared DCPD was done under inert atmosphere, to prevent oxidation. For the preparation of DCPD with rubbers we used a two liter hermetic reactor with internal heating and mechanical stirrer. Rubber was dissolved in DCPD by heating near 150°C during 25 hours under inert atmosphere. Second generation Grubbs catalyst was used for the polymerization and the polymerization process took place in a metal hand-made mold with internal heating by two thermostats. Two monomer modifications were made using the synthetic rubbers Buna 3950 and Royalene 563.

The polymerization process consists of two steps – the first step is the same for each sample, the second step is different. After the mold was filled with monomer, the lower plate of the mold was heated to 70°C and the upper plate to 50°C during 20 minutes. We expect the initiation of the polymerization process during this step. After 20 minutes the temperatures were increased for the second step. The following three temperature settings were used: 1) 100°C lower plate – 80°C upper plate 2) 120°C lower plate – 100°C upper plate 3) 140°C lower plate – 120°C upper plate. Each temperature setting was used for 30 minutes and after that the mold was cooled by air, during about 60 minutes. As a result, for each type of used monomer (pure DCPD, DCPD with Royalene 563 and DCPD with Buna 3950) three samples (plates) were made with different “second stage” temperatures. Also, in all experiments the same second generation Grubbs catalyst⁸ ratio (1:15000) used.

After polymerization sample plates of polymerized DCPD were obtained and samples were taken from each plate for DSC analysis DCS-analysis was done using a Netzsch DCS 200 F3 Maia device. Each sample was measured in inert atmosphere from 25°C till 300°C with 10K per minute heating rate. After first DCS printing and cooling, a second DSC printing was done in the same conditions (Fig. 2).

3. Results and Discussion

As a result for each sample, we obtain a complex peak on the DCS curves, after the glass transition temperature peak. This peak can tell us that second step of polymerization is not complete and after additional heating of the pDCPD, more crosslinking between polymer chains can be created. The area of this peak is different for each sample and can tell us how much energy is produced when we initiate second step polymerization by heating in the DCS-device (Table 1).

Table 1. Complex peak area on DSC curves

Monomer	80/100, J/g	100/120, J/g	120/140, J/g
Pure DCPD	31.20	34.56	28.59
DCPD + Buna 3950 (5%)	22.42	17.41	64.19
DCPD + Royalene 563 (5%)	39.70	53.51	55.86

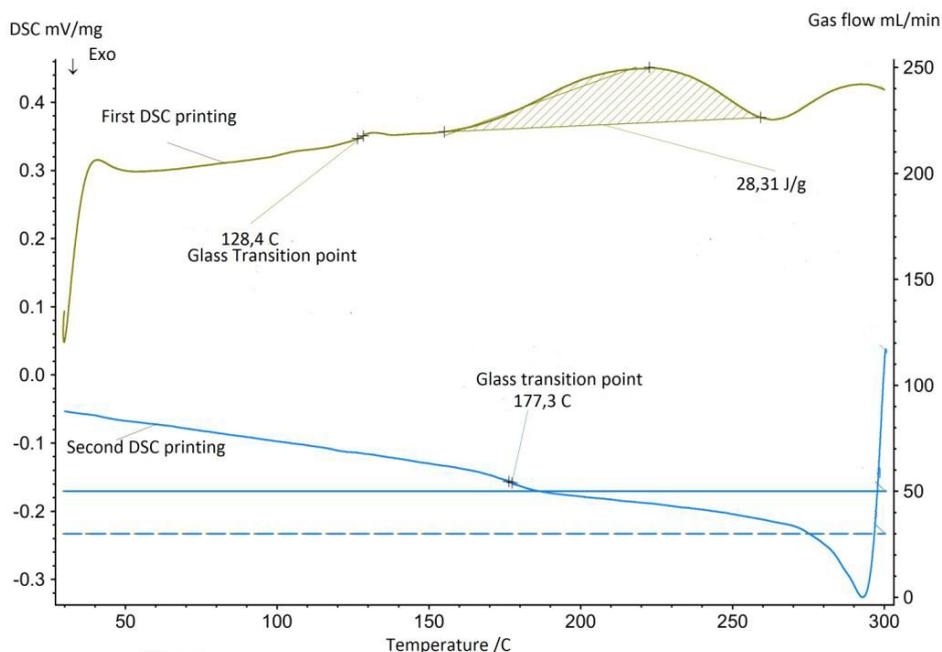


Fig 2. One of the DSC curves (100/120 temperature setting)

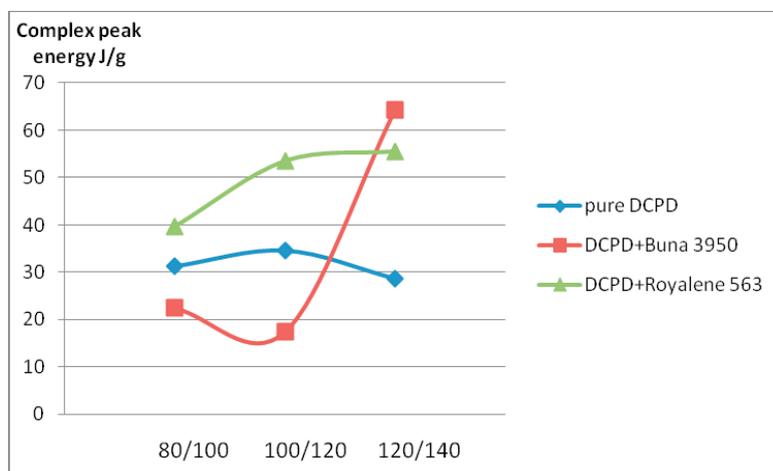


Fig 3. Influence between complex peak area and temperature settings

Second printing DCS curves don't have complex peak and have glass transition temperature always near 170-180°C. In our work second printing used only for be sure that complex peak totally disappears

4. Conclusion

We can see that the correlation between complex peak energy and temperature setting is not so obvious (Fig.3). The influence of the rubbers on complex peak energy is not evident, but we assume that it can be linked to the influence of the formation of oligomers. We can also state that the temperature setting used was too low for total polymerization of pure DCPD or DCPD with rubbers. To verify this, further analysis is required whereby physical testing and the correlation with glass transition temperature has to be included.

Acknowledgments

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