

## Thermal Properties of 1,3-Cyclohexadiene Polymers

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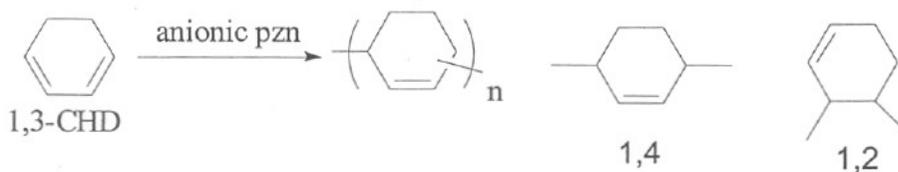
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### ABSTRACT

The thermal properties of 1,3-cyclohexadiene polymers have been studied. The glass transition temperatures ( $T_g$ ) of PCHD polymers are dependent on their molecular weight and microstructures (1,4/1,2 ratios). PCHD with lower 1,4/1,2 ratio shows higher  $T_g$  than those with higher 1,4/1,2 ratio with similar molecular weight. In some of the DSC traces of PCHD polymers with high 1,4 ratio (~95%), a peak similar to a crystalline peak appears. This was confirmed by X-ray diffractions. However, the exothermic peak disappeared on repeated runs and it did not act like crystallization when it was treated isothermally. Those peaks may be from higher order structures other than crystallizations. The thermogravimetric analysis results of those samples were also discussed.

### INTRODUCTION

Hydrocarbon polymers containing alicyclic structure repeated units in the main chain has been attracting great interests from both basic and practical points, because a dramatic improvement of thermal, chemical stabilities and mechanical strength is expected for such polymers as compared to conventional polyolefins. Poly(1,3-cyclohexadiene) (PCHD) is of particular interest since it has six-member rings directly connected to each other in the main chain. Moreover, there are two possible microstructures in the polymer chain, just like the polymers from other conjugate 1,3-dienes (Scheme 1). However the elucidation of the properties of 1,3-cyclohexadiene polymers has been hindered because of the difficulty in synthesizing well-defined samples. There are many reports about the synthesis of PCHD with virtually all kinds of polymerization techniques. The obtained polymers were usually of low molecular weight and broad distribution. Recently, the synthesis of PCHD polymers with different microstructures in a controlled manner has been achieved (1,2). The solution properties of PCHDs depend strongly on their microstructures (3). The phase behaviors of copolymers containing PCHD blocks are also different from other diene copolymers. For example, PS-*b*-PCHD block copolymer with 40 vol % of PCHD formed novel core-shell structure with very good long range order (4). While PS-*b*-PI block copolymer with similar compositions only formed lamella structures. The microstructures of the PCHD block also play a major role in the phase separations in PCHD block copolymers (5).



Scheme 1 Microstructures of PCHD

... the thermal properties of various ... microstructures and the thermal behaviors is also discussed.

## EXPERIMENTAL

The PCHD samples were prepared by anionic polymerizations by using two initiating systems as reported earlier (1,2). The *sec*-butyllithium (*sec*-Diazabicyclo[2,2,2]octane (DABCO) complexes resulted in high 1,4/1,2 ratio (~9:1) polymer chain. While *n*-butyllithium (BuLi)/N,N,N',N'-tetramethylethylenediamine initiating system gave lower 1,4/1,2 ratio in the main chain (~50/50). The molecular weight of the polymers was determined by size exclusion chromatography (SEC, Polymer Lab 12000 equipped with refractive index and light scattering detectors in chloroform or tetrahydrofuran (THF). The microstructures of the samples were obtained on a Bruker Avance 400 MHz spectrometer in deuterated chloroform.

Thermal analysis of PCHD samples was carried out using two characteristic techniques: thermal gravimetric analyzer (TGA) and differential scanning calorimetry (DSC). First, the thermal decomposition properties were studied using a TA Instruments TGA 2050 thermal gravimetric analyzer. Nitrogen was used as the purge gas for all the samples in a balance. Approximately 2-15 mg of PCHD samples were used for each analysis. The samples were heated up to 1073 K using a heating rate of 20 K min<sup>-1</sup>. Thermal Advantage software installed on an IBM computer system controlled the instruments. The data was analyzed using Universal Analysis software on the same computer system.

The glass transition temperatures,  $T_g$ , were measured for PCHD samples by calorimetry using standard differential scanning calorimetry (DSC) and were determined by midpoint of the flow rate between solid and melt phases. DSC measurements were performed using a TA Instruments DSC Q1000 and Mettler Toledo 820 differential scanning calorimeter. Nitrogen was used as the purge gas at a flow rate of 50 ml min<sup>-1</sup>. Approximately 2-15 mg of PCHD samples was used for each analysis. For standard DSC, the samples were heated from 183 K to 473 K at the rate of 20 K min<sup>-1</sup> using aluminum pans. The instruments were controlled using Thermal Advantage software installed on an IBM computer system. The data were analyzed using Universal Analysis software on the same computer system.

## RESULTS AND DISCUSSION

Table 1 shows the characteristics of the samples used in this study. The glass transition temperatures ( $T_g$ ) of those samples are also listed in Table 1. From this table we can see that  $T_g$  increases with the increase of molecular weight for polymers with the same microstructures (run 1-3). According to Fox and Flory (6), the relationship of  $T_g$  and number average molecular weight ( $M_n$ ) can be expressed by the following empirical equation:

$$T_g = T_g^\infty - K / M_n$$

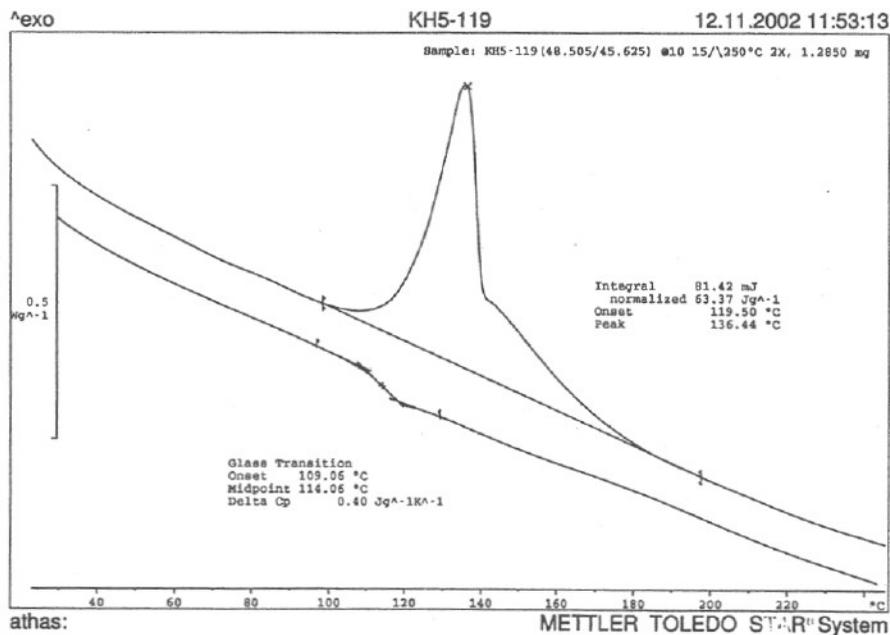
where  $T_g^\infty$  is  $T_g$  of the polymer have infinite molecular weight.  $K$  is a constant unique to each polymer and it is reported that large  $K$  indicated rigid polymer chain and it is a constant only in certain molecular weight range (7). From the  $T_g$  in Table 1 we can see the  $K$  is not a constant. This may arise from a narrow molecular weight range. Detailed study of this relationship is underway and will be published in forthcoming full paper. Table 1 also indicated

the  $T_g$  is lower for samples with high 1,4/1,2 ratios (run 3 and 4), which is confirmed by Natori (8).

**Table 1** Characteristics of PCHD polymers

Run	Sample	$M_n$ (Kg/mol)	PDI	1,4/1,2 (NMR)	$T_g$ (°C)
1	KH7-052	3.1	1.10	95/5	80
2	KH6-112	6.2	1.11	95/5	102
3	KH5-119	11.6	1.05	94/6	114
4	KH5-137	11.2	1.07	49/51	120

Figure 1 shows the DSC traces of a PCHD sample with molecular weight around 11.6 kg/mol (KH5-119). An exothermic peak at 136°C (399 K) appeared during the first run with 5.13 kJ/mol of heat involved, which disappeared upon repeated runs. This peak might be from crystallization or stress releasing process. However, the amount of heat involved is too big to be stress release and too small to be a crystallization of 100% crystal. Of course partial crystallization is possible. The X-ray diffraction indeed shows a broad peak around  $2\theta = 15^\circ$ . When we tried to isothermally treat the sample, we could not find any crystallization. We did not see this kind of peak in all samples. Combined with other evidences, we suggest that this peak is from higher order structures (3). Figure 2 shows the DSC traces (second run) of other samples.



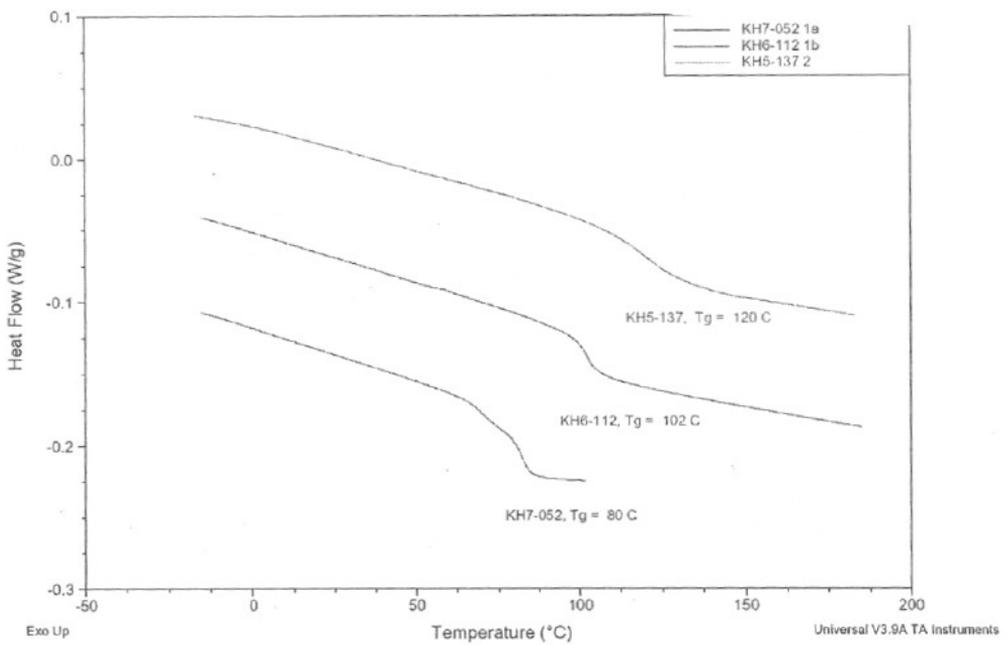


Figure 2 DSC trace of various PCHD

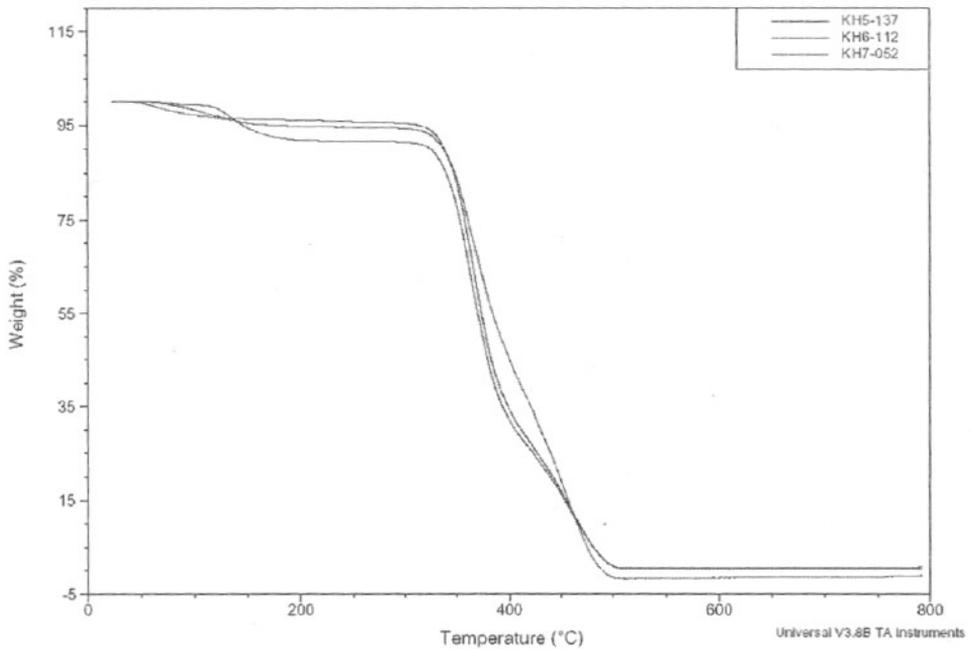


Figure 3 TGA trace of various PCHD

Figure 3 shows thermogravimetric analysis (TGA) traces of various PCHD in nit environment. Initial degradation around ~100°C is observed in all samples. Williamson et al

found this and attributed it to depolymerizations (9). All the samples started to decompose around 350°C. The process is faster for high 1,4/1,2 ratio sample than that for lower 1,4/1,2 ratio sample. When the temperature reaches around 380°C, the process reverses. This suggests that carbonization happened in high 1,4/1,2 ratio PCHDs. This is also confirmed by the residual material left after 500°C.

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