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Characterization of Polycyclohexene by High Field ^{13}C-NMR Spectroscopy

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Summary

^{13}C NMR spectrum of polycyclohexene is recorded at 50.5 MHz and interpreted in terms of its different stereoisomers. The ratio of threo to erythro forms in the polymer is 2:1. The spectrum is also sensitive to tacticity of the polymer chain.

Introduction

Although cycloolefins can easily homopolymerize in the presence of transition metal organometallic catalysts to high molecular weight polyalkenamers via a ring-opening polymerization process, they are generally inert toward homopolymerization by the conventional addition (double bond opening) method(1). Only in special cases where the internal bonds are constituents of highly strained ring systems have they been homopolymerized(2)-(5).

Several unsuccessful attempts have been made to homopolymerize cyclohexene either by a ring-opening or a double bond-opening process(6). This failure has been attributed to the high ring stability. Nevertheless, some oligomers have been obtained from cyclohexene in the presence of a BF_3/HF initiator(7) under extreme conditions(8) (300°C, 65,000 atm), or by the catalytic action of the $WCl_6/ROH/C_2H_5AlCl_2$ system(9).

A few years ago, one of us reported(10),(11) that $Re(CO)_5Cl$ catalyst with $C_2H_5AlCl_2$ co-catalyst promoted the homopolymerization of cyclohexene via the double bond-opening mechanism to a relatively high molecular weight polymer(M_w = 2,500). Some preliminary physical and chemical tests for the structural characterization of polycyclohexene have revealed(11) that the polymer product is saturated and the rings are preserved. Here we investigate systematically the structure of polycyclohexene, because of its novelty, by high field ^{13}C-NMR spectroscopy.

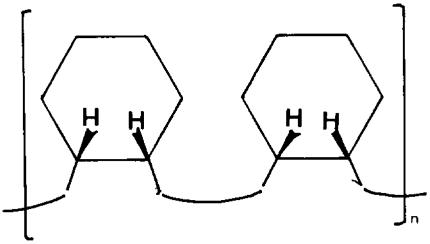
Experimental

The polymer was prepared by mixing 0.1 mole cyclohexene, 1 mmole $Re(CO)_5Cl$ and 2 mmoles $C_2H_5AlCl_2$ in 20 ml chlorobenzene at 110°C for 24 hours. More experimental details are given in a previous article(11).

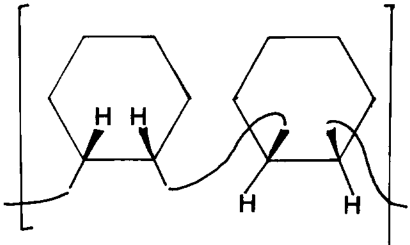
The NMR spectra were recorded on a Varian XL-200 spectrometer with a carbon frequency of 50.3 MHz. The polymer sample was observed as a solution in $CDCl_3$ (0.5 g in 2.5 ml $CDCl_3$) at 20°C and 55°C with TMS as internal standard. The flip angle was 45 degrees and a digital resolution of 0.3 Hz was used. The relaxation time(T_1) was measured by the inversion recovery method and found to have values in the range 0.6 - 1.0 s. For quantitative analysis, the nuclear Overhauser enhancement was suppressed by operating in the gated decoupling mode in which the protons were irradiated only during the processing of free induction decay. The decoupler was off during pulse and delay time. A pulse delay time of 10 s ($>5T_1$) was also used.

Results and Discussion

Polycyclohexene contains cyclohexane rings incorporated into the main chain and posseses two chiral centers and presents a combination of isomerisms connected with ring geometry and tacticity. The four possible stereo regular forms are shown below. The thick and thin lines at the 1- and 2- positions represent bonds above and below the plane of the ring respectively. The erythro structures (I, II) have a cis configuration of the polymer chain bonds entering and leaving each ring, while the threo structures (III, IV) have a trans configuration of the polymer chain bonds entering and leaving the ring. Polycyclohexene also exhibits tacticity; for example structures I and II are the erythrodisyndiotactic and erythrodiisotactic forms respectively. On the other hand, the threo structures III and IV may be threodiisotactic and threosyndiotactic forms respectively.



I



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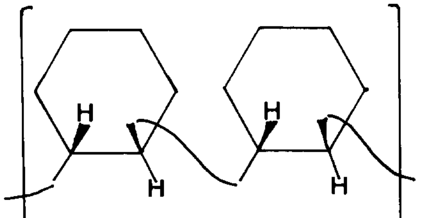
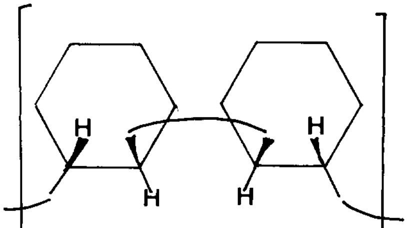


III



IV

The ^{13}C NMR spectrum of polycyclohexene obtained at 20°C is shown in figure 1. The spectrum at 55°C is similar, indicating that there is no conformational change in the 20 - 55°C range. The olefinic carbon signals were absent in the spectrum. The first point to be resolved is whether polycyclohexene is made of 1,2-cyclohexene units or a combination of

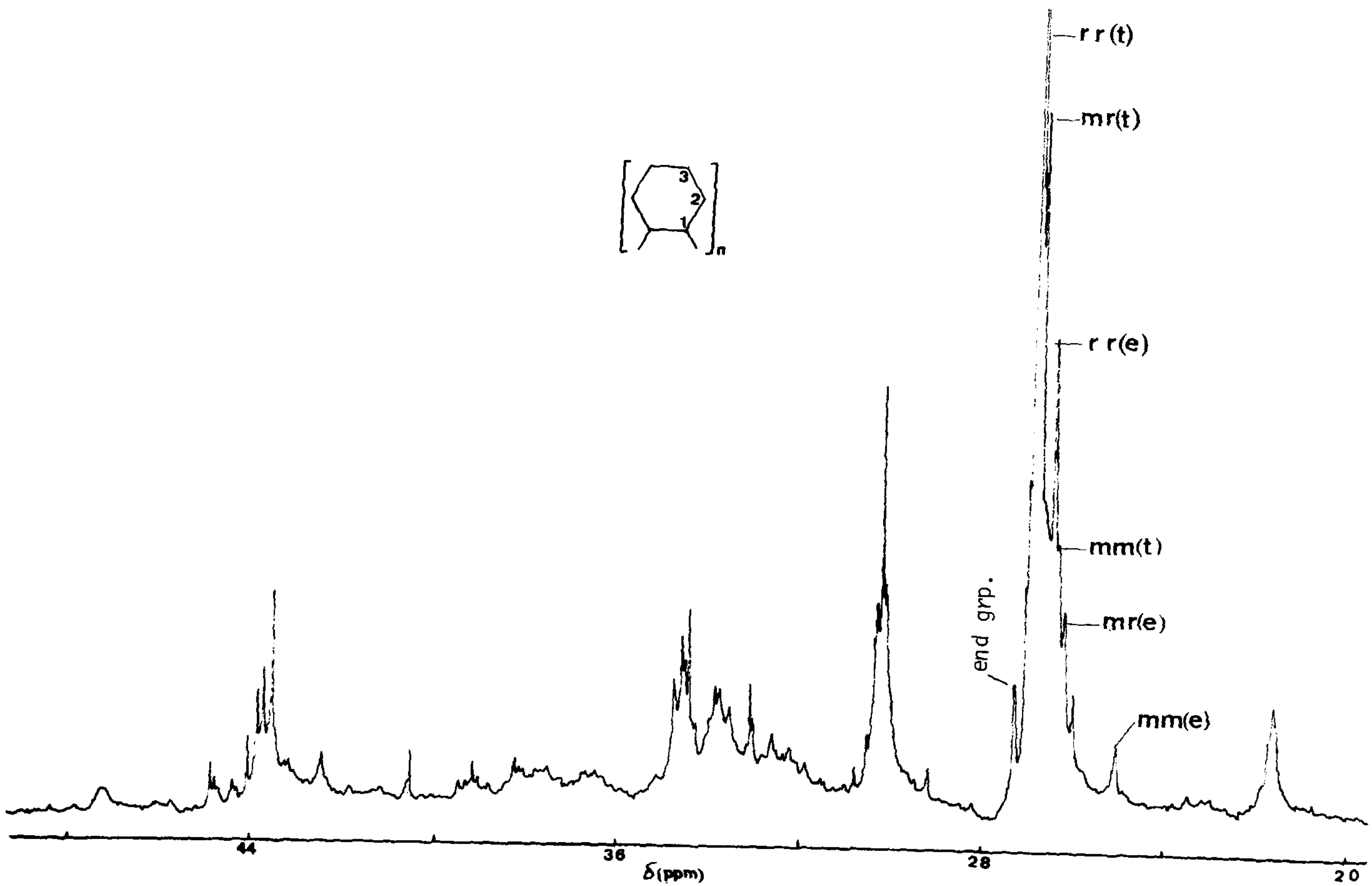


Figure 1. Proton decoupled ^{13}C NMR spectrum of Polycyclohexene at 20°C.

1, 2-, 1, 3- and/or 1, 4- repeating units. Signal assignments are based on the reported(12) shifts of 1, 2- dimethylcyclohexane, 1, 3- dimethylcyclohexane and 1, 4- dimethylcyclohexane. Examination of the ^{13}C NMR spectrum of the polymer shows strong peaks at about 27 ppm, however, 1, 4-dimethylcyclohexane has no peaks at this region. The 1,3- repeating units are also absent in the structure of the polymer because, on the basis of the observed chemical shifts and intensities of the polymer peaks, 1,3 substitution would require one-half intensity around 35-45 ppm and one-sixth intensity at 27 ppm. The cis- and trans- 1,2-dimethylcyclohexane shows peaks(12) for C_1, C_2 and C_3 in the range 35.0-40.1, 32.1-36.6 and 24.5-27.3 ppm, respectively. The polymer spectrum has three equal intensity regions 35.5-44.0, 30.0-35.0 and 22.0-27.0 ppm corresponding to C_1, C_2 and C_3 carbons respectively of a 1,2 substituted cyclohexane units. Therefore the spectrum fits fairly well with the 1,2 substituted cyclohexane structure for the polymer and rules out any major contributing structures of 1,3 or 1,4 cyclohexane repeating units. These results suggest that no double bond isomerization of cyclohexene has occurred during the addition polymerization process in the presence of the $Re(CO)_5Cl/C_2H_5AlCl_2$ catalyst system.

The different stereoregular forms of polycyclohexene were also established by quantitative ^{13}C NMR spectroscopy. The assignments are summarized in Table 1 and are based on the shifts of cis- and trans- 1,2-dimethylcyclohexane. Of the two bonds entering and leaving the ring in the erythro configuration, one is equatorial and the other is axial. The axial bond substituent has a γ-gauche interaction(13) with C_2 and C_3, bringing about shielding of these two carbons. Hence the C_2 and C_3 in the erythro form appear at a higher field than the corresponding carbons in the threo form where the γ-gauche interaction is absent. The intensity ratio of the threo to erythro, calculated from C_1 and C_2 carbon regions was 1.91:1 and 2.12:1 respectively. The threo form is more abundant as expected from steric considerations.

Table 1. ^{13}C NMR chemical shifts(ppm) of polycyclohexene

C_1	threo	42.0 - 44.0	
	erythro	35.5 - 41.0	
C_2	threo	32.0 - 35.0	
	erythro	30.0 - 31.5	
C_3	threo	26.9	rr
	threo	26.8	mr
	threo	26.5	mm
	erythro	26.6	rr
	erythro	26.4	mr
	erythro	25.3	mm

The C_3 region shows fewer peaks than that of the other two carbons. This is in keeping with the most distant position of the C_3 from the points of the linkage. The C_3 region is sensitive to triad tacticity on the erythro and threo configurations. The Dreiding model of polycyclohexene shows large steric crowding in the meso form compared to the racemic form. This would cause the meso resonances to appear at slightly higher field and to have lower intensities than that of the racemic. Therefore the weak high field signals are assigned to the mm configuration (Table 1). The steric crowding is very severe for the meso in the erythro configuration and hence the mm triad is assigned the weak signal at 25.3 ppm rather than the slighltly more intense highest field peak at 21.9 ppm. In methyl cyclohexane, the C_3, C_4 and C_5 carbon signals appear(12) at 27.4 ppm and based on this the signal at 27.3 ppm in the polymer spectrum can be assigned to the corresponding carbons in the end group of the polymer chain.

The C_1 and C_2 regions show a large number of peaks with a great deal of spread in the chemical shifts, revealing atleast tetrad tacticity. The γ-gauche interactions are more pronounced for the C_1 and C_2 in the m dyads. At this point we are unable to assign the individual peaks in these two regions.

Acknowledgements

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