

NOTES

Appearance of New Structures of Polyallene in the Solid State at Low Temperatures as Observed by Variable-Temperature High-Resolution ^{13}C NMR Spectroscopy

Kyung Hoon MIN,* Hiromichi KUROSU,* Isao ANDO,*
Takakazu YAMAMOTO,** and Takaki KANBARA**

* *Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan*

** *Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Midori-ku, Yokohama 227, Japan*

(Received January 17, 1992)

KEY WORDS Polyallene / Solid State ^{13}C CP/MAS NMR / Structure /

In our previous paper,¹ we observed high-resolution ^{13}C NMR spectra of polyallene $[-(\text{CH}_2\text{C}(\text{=CH}_2))_n-]$ in the solid state at temperatures from room temperature to 100°C and found that the ^{13}C resonance lines of the noncrystalline, orthorhombic, monoclinic and paracrystalline forms are shifted from one another. On the basis of these peak assignments the structural change was studied over the course of the temperature variation. From these studies it has been suggested that the transition energies among the crystalline structures are very low.

In the present work, we attempt to study the structural change of polyallene in the solid state at low temperatures from -120°C to room temperature by means of variable temperature (VT) ^{13}C cross polarization/magic angle spinning (CP/MAS) NMR.²

EXPERIMENTAL

Polyallene (sample A) was prepared by Ziegler-type catalyst as described previously. Structural characterization will be described below.

^{13}C NMR spectra of polyallene in the solid

state at low temperatures were observed from -120°C to room temperature with a JEOL JNM-GSX270 NMR spectrometer operating at 67.5 MHz with a VT CP/MAS accessory. Contact time was 2 ms and repetition time was 5 s. The sample was contained in a cylindrical ceramic rotor. The rotor was spun at about 2—4 kHz. The spectral width was 27 kHz, and 8 K data points were used. The number of accumulations was 600—1000. ^{13}C chemical shifts were calibrated indirectly from adamantane at high field (29.5 ppm) relative to TMS (tetramethylsilane).

The DSC measurements were performed with a Perkin-Elmer DSC calorimeter.

RESULTS AND DISCUSSION

^{13}C CP/MAS NMR spectra of polyallene in the solid state at temperatures from -120°C to room temperature are shown in Figure 1. The peaks can be assigned to the >C= , $\text{CH}_2\text{=}$ and $-\text{CH}_2-$ groups from downfield to upfield. Further, each signal at room temperature consists of the main peak, a small peak and a shoulder peak and these are assigned to orthorhombic (O), monoclinic (M) and non-

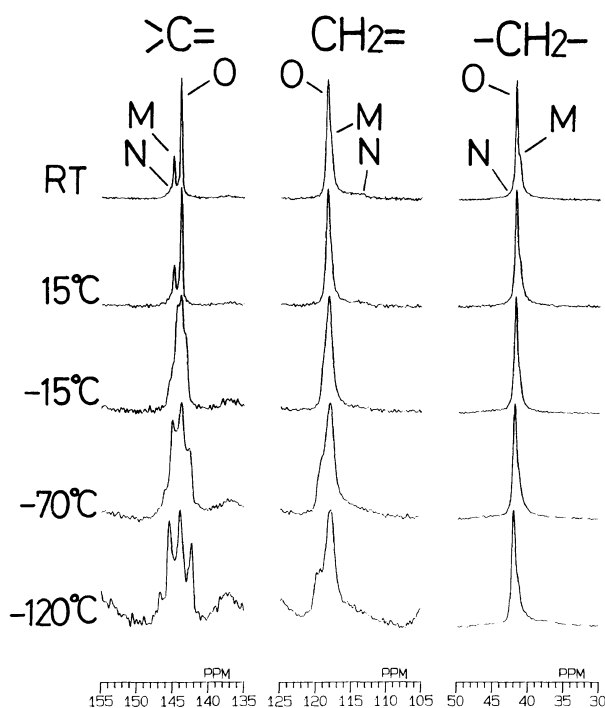


Figure 1. ^{13}C CP/MAS NMR spectra of polyallene in the solid state as a function of temperature.

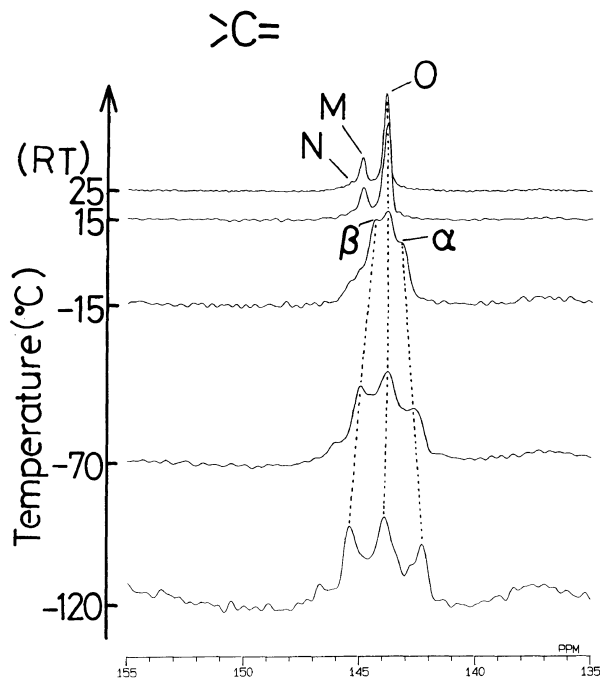


Figure 2. Expanded ^{13}C CP/MAS NMR spectra of the $>\text{C}=\text{O}$ carbon region of polyallene in the solid state as a function of temperature.

crystalline (N) structures, respectively, as described previously¹ with the aid of X-ray diffraction study.³ It is shown from Figure 1 that the $\text{CH}_2=$ and $-\text{CH}_2-$ carbon signal patterns do not greatly change as the temperature is decreased, but that the >C= carbon signal pattern does markedly change. For convenience, the >C= signal is expanded in Figure 2. It is apparent that in the ^{13}C signal at -15°C new two peaks appear at 143.2 and 144.3 ppm besides the orthorhombic and monoclinic peaks; these are designated as α and β , respectively. On the other hand, in the DSC thermogram within this temperature range, no structural transition was observed. This shows that structural changes slowly occur with decreasing temperature. As shown in the expanded spectra of the >C= carbon as a function of temperature, the orthorhombic and monoclinic peaks at -15°C can be identified. From these results, it can be said that in the low temperature range, orthorhombic and monoclinic structures, and new structures coexist. With decreasing temperature, peak β largely shifts downfield and overlaps with the monoclinic peak at -70°C . At temperatures

of -70 and -120°C , the >C= signal clearly becomes three peaks. Also, peak α largely shifts upfield. From these results, it can be said that the peaks α and β may come from meta-stable structures which are very sensitive to temperature. As seen from the observed spectra the orthorhombic and monoclinic structures change to these structures gradually as the temperature is decreased from room temperature. These structures are not identified by X-ray diffraction studies at this stage, which were not carried out at low temperatures. In order to clarify these structures, we will expect the X-ray diffraction study at low temperatures.

REFERENCES

1. K. H. Min, H. Kurosu, I. Ando, T. Yamamoto, and T. Kanbara, *Macromolecules*, **24**, 2011 (1991).
2. For example, a) R. A. Komoroski, Ed., "High Resolution NMR Spectroscopy Synthetic Polymers in Bulk," VCH Publishers, Deerfield Beach, Florida, 1986; b) I. Ando, T. Yamanobe, and T. Asakura, *Prog. NMR Spectroscopy*, **22**, 349 (1991).
3. H. Tadokoro, Y. Takahashi, S. Otsuka, K. Mori, and F. Imaizumi, *Polym. Lett.*, **3**, 697 (1965).