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Transmission Electron Microscopic Observation of Nascent Polypropylene Particles Using a New Staining Method

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ABSTRACT: The internal structure of nascent polypropylene particles was observed in a transmission electron microscope by using the two-step staining method employing 1,7-octadiene and osmium tetraoxide (OsO_4). The particles are agglomerates of many primary polymer particles with diameters of 0.2–0.35 μm. The size of the primary polymer particles is in good agreement with that predicted from the polymer yield and the size of the original catalyst crystallites but considerably smaller than that of polymer globules on the surfaces of the polymer particles, ca. 1 μm in diameter, observed by scanning electron microscopy. In the core of the individual primary polymer particles there exist one or a few catalyst crystallites, the size of which agrees with that of the original catalyst crystallites and from which titanium can be detected by X-ray microanalysis. These findings reveal that the polymer globules that have been considered as primary particles are not primary but secondary particles.

Introduction

Ziegler–Natta polymerization using heterogeneous catalysts is the only major process for the production of highly stereospecific polypropylene, in which δ-$TiCl_3$ and $TiCl_4/MgCl_2$-supported catalysts are mainly used as the industrial catalysts. The typical catalysts are the 10–30-μm particles consisting of loosely bound agglomerates of fine catalyst crystallites, several tens to several hundreds of angstrom in diameter.[1-5] The growth of the polymer particles on catalysts[2,6-11] and their architecture[1,12-14] have aroused much interest widely. Mackie and co-workers showed that the nascent polymer particles produced by such catalysts replicate the original catalyst morphology.[15] This finding means that the morphology of the polymer particle can be controlled by the catalyst morphology, which is very important from the industrial point of view. Hock observed the internal structure of the nascent polymer particles by electron microscopy and found that they are agglomerates of many thousands of fine polymer globules ca. 0.5 μm in diameter.[1] Furthermore Graff and co-workers reported good agreement between the size of the catalyst crystallites and that calculated from the size of the observed polymer globules.[12]

From these experiments it has been generally accepted that the nascent polymer particle replicates not only the external structure of the original catalyst particle but also its internal structure. However, in spite of such extensive efforts, the relationship between the primary polymer particle and the primary catalyst crystallite is still not completely elucidated due to the lack of a suitable observation method. The knowledge of this relationship would lead to a good understanding of the physicochemical process of the Ziegler–Natta polymerization. Scanning electron microscopy (SEM) is not pertinent to this purpose because of the inherent disadvantage that the catalyst crystallite embedded within the polymer particles cannot be observed. In contrast, transmission electron microscopy (TEM) is obviously a powerful method for this purpose. However, an adequate staining method has not so far been developed for the visualization of the primary polymer particles. In a previous paper we showed the versatility of the two-step staining method using 1,7-octadiene and OsO_4 for visualization of saturated rubbers.[16] This method basically utilizes a selective penetration of 1,7-octadiene. Therefore, this method may be used for the selective stain of the surface of the primary polymer particles. This paper describes the architecture of the nascent polypropylene particles observed in a transmission electron microscope by using this staining method.

Experimental Section

Catalyst. δ-$TiCl_3$ was prepared by reduction of $TiCl_4$ with $Al(C_2H_5)_2Cl$ and treatment of the reduced products with diisoamyl ether and then with $TiCl_4$. $TiCl_3$ AA grade was supplied by Toho Titanium Co. Ltd. The $Ti(OR)_{0.5}Cl_{3.5}/MgCl_2$-supported catalyst was prepared as follows. $MgCl_2$ as a support was synthesized from *n*-butylmagnesium chloride and $SiCl_4$ and then treated with ethyl benzoate. The support thus obtained was treated with $Ti(OR)_{0.5}Cl_{3.5}$ (OR: *o*-cresoxy).

Polymerization. Polymerization was carried out in a 5-L stainless steel autoclave in liquefied propylene or *n*-heptane. The polymerization was terminated by flashing out propylene. The polymer particles for SEM observation were treated with methanol for 1 h at room temperature and filtrated. Then it was treated with *n*-heptane for 5 min at room temperature, filtrated, and dried in a vacuum oven. The polymer particles for TEM observation were used without any treatment.

Electron Microscopic Observation. The polymer samples for SEM observation were coated with platinum by a conventional sputtering technique. The samples for TEM observation were immersed in purified 1,7-octadiene at room temperature in an atmosphere of argon for 2 h. After filtration, liquid 1,7-octadiene was removed by flowing argon for ca. 10 min. Then the samples were stained with 1% aqueous solution of OsO_4 for 3 h at 60 °C and sectioned at −80 °C by means of ultramicrotome equipped with a glass knife. The sections were 500–1000 Å thick. The specimens were examined in a Hitachi H-500 electron microscope equipped with SEM device and energy-dispersed X-ray microanalyzer (EDX).

X-ray Diffraction. X-ray diffraction measurement was carried out with a Shimadzu X-ray diffractometer VD-2 using scintillation counter and pulse height analyzer. Ni-filtrated Cu Kα radiation was used. The crystallite sizes of $TiCl_3$ were calculated from the breadth of the diffraction peaks,[21] (003) (at $2\theta = 15.0°$ for δ-$TiCl_3$ and $TiCl_3AA$) and (300) (at $2\theta = 51.5°$ for δ-$TiCl_3$ and 51.8° for $TiCl_3AA$) lines by Scherrer's equation after correction had been made according to Warren's method.[17] Similarly, the crystallite size of the $Ti(OR)_{0.5}Cl_{3.5}/MgCl_2$-supported catalyst was calculated from the (003) at $2\theta = 15.0°$ and (110) at 50.1° lines.

Results and Discussion

The catalysts subjected to the present experiments are listed in Table I, where the dimensions of the catalyst crystallites are also shown. The polymer samples are shown in Table II, and the SEM photographs of the polymer particles are shown in Figures 1 and 2. Those polymer particles show similar surface structure, consisting of aggromerates of the fine polymer globules about 1 μm in diameter irrespective of the catalysts. Some fibrils having diameters of about 0.1 μm are seen in the polymer

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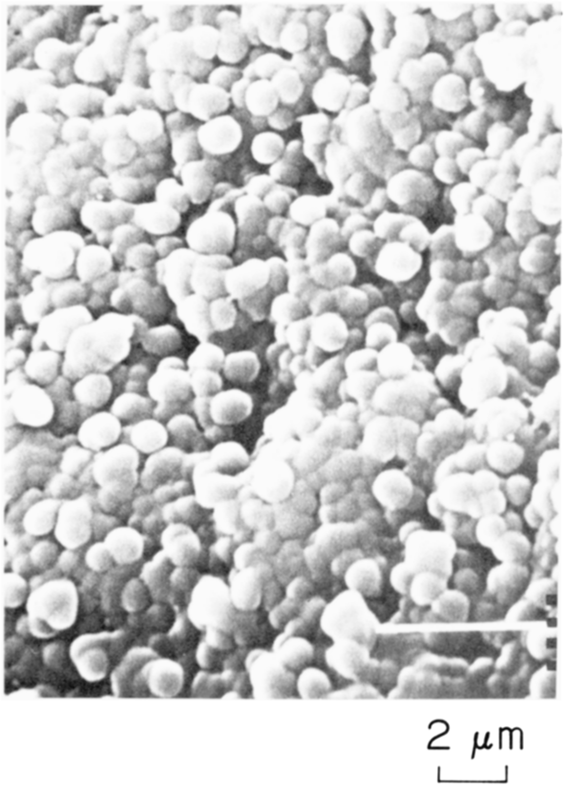

Figure 1. SEM photograph of the surface of sample A prepared with the δ-$TiCl_3$ catalyst system.

Table I
Characteristics of Catalysts

catalyst	av particle size, μm	cryst size, Å	polymeriz activity, g of polymer/g of catalyst
δ-$TiCl_3$	19	108[c] 185[d]	1100[a]
$TiCl_3AA$	30	120[c] 100[d]	1200[a]
$Ti(OR)_{0.5}Cl_{3.5}/MgCl_2$-supported catalyst	12	40[e] 30[d]	19600[b]

[a] Polymerization was carried out at 65 °C for 2 h in liquefied propylene. [b] Polymerization was carried out at 65 °C for 1 h in liquefied propylene by adding methyl *p*-toluate as an external donor. [c] D_{300}. [d] D_{003}. [e] D_{110}.

Figure 2. SEM photograph of the surface of sample B prepared with the $TiCl_3AA$ catalyst system.

particles polymerized with the $TiCl_3AA$ catalyst system. These fibrils are similar to those observed in nascent polyethylene particles by Graff et al.;[12] these fibrils may be formed by cold-drawing a part of a crust of the individual polymer particles. In addition, one can observe some fibrous structures having diameters of about 1 μm in which some polymer globules are probably linked like a rosary. They seem close to those reported by Wristers.[13] These morphological features are similar to those reported previously though the size of the polymer globules is slightly different.[1,12,13] These polymer globules, as described above, have been generally accepted to be the primary polymer particles, each of which will grow surrounding the primary catalyst crystallite.[12,18] When this view is valid, an average diameter of the polymer globules (D) can be calculated from that of the catalyst crystallites (d) and the polymer yield (Y, grams of polymer/grams of catalyst) by the following equation:

$$D = d((\rho_{\mathrm{cat}} Y/\rho_{\mathrm{pp}}) + 1)^{1/3}$$

where ρ_{cat} and ρ_{pp} are the densities of the catalyst crystallite and polypropylene. 2.7 g/cm^3 is taken as ρ_{cat} for $TiCl_3$ and 0.9 g/cm^3 as ρ_{pp}. The average diameters thus calculated are shown in Table III. In the case of sample A polymerized with the δ-$TiCl_3$ catalyst system, the observed average size of the polymer globules, about 1 μm in diameter, is approximately 4-fold larger than that calculated from the size of the catalyst crystallite. In the case of sample B prepared with the $TiCl_3AA$ catalyst system, the observed size of the polymer globules is also 4–5-fold larger than expected. These results imply that the polymer globules seen on the surfaces of the polymer particles are not the primary polymer particles.

To answer this question, we observed the internal structure of the polymer particles by TEM. Figure 3 shows a TEM photograph of the portion near the surface of sample A prepared with the δ-$TiCl_3$ catalyst system. One can see the agglomeration structure within the polymer particles. This picture resembles Figures 1 and 2 very

Table II
Polymer Samples

		polymerization[d]					
sample	catalyst syst	Ti/Al/donor, mmol/L	temp, °C	press., kg/cm^2	time, h	medium	yield,[e] g/g
A	δ-$TiCl_3$	0.15/13[a]/0	65	29	5	propylene	2030
B	$TiCl_3AA$	0.13/13[a]/0	65	29	5	propylene	2140
C	$Ti(OR)_{0.5}Cl_{3.5}/MgCl_2$-supported catalyst	0.010/4.4[b]/0.96[c]	70	7	1.5	heptane	8000

[a] $Al(C_2H_5)_2Cl$. [b] $Al(C_2H_5)_3$. [c] Methyl *p*-toluate. [d] Polymerizations were carried out in a 5-L autoclave. [e] Grams of polymer/grams of catalyst.

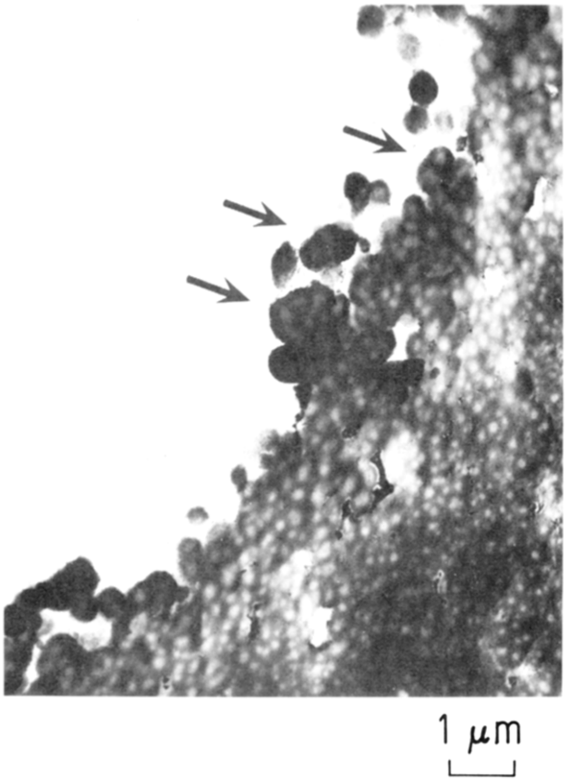

Figure 3. TEM photograph of sample A prepared with the δ-$TiCl_3$ catalyst system.

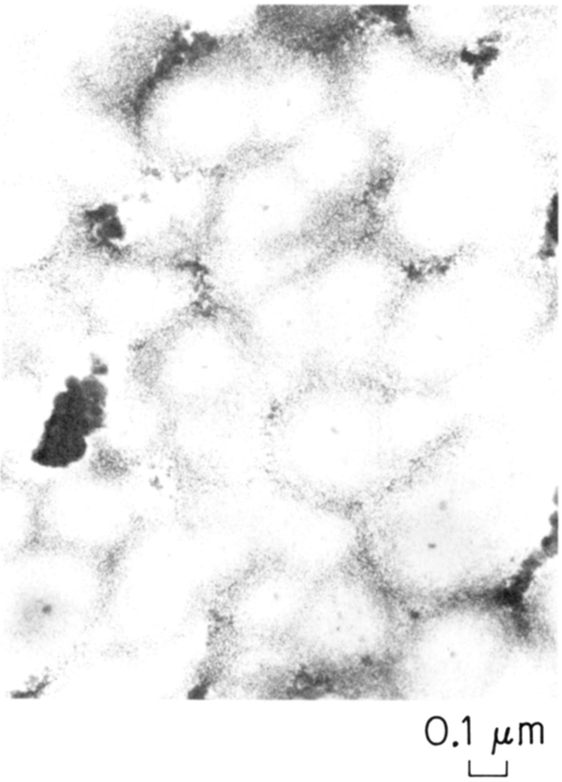

Figure 4. TEM photograph of sample A prepared with the δ-$TiCl_3$ catalyst system.

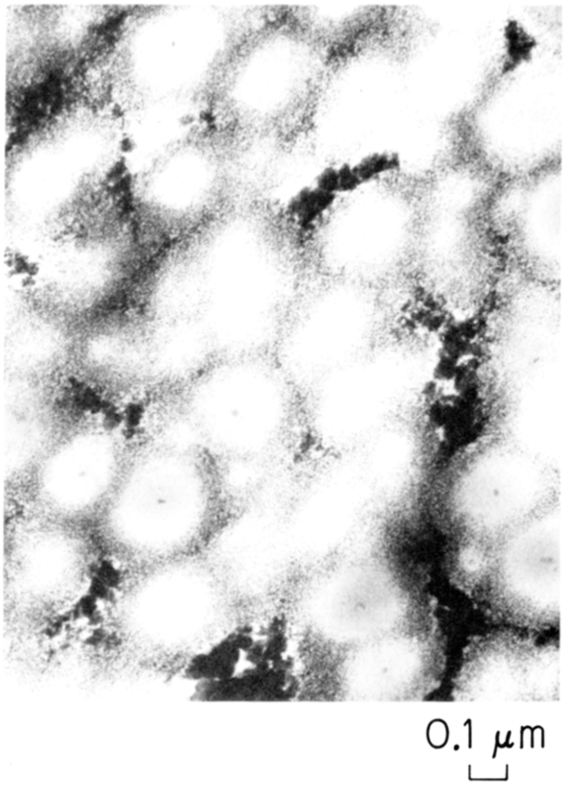

Figure 5. TEM photograph of sample B prepared with the $TiCl_3AA$ catalyst system.

Figure 6. TEM photograph of sample C prepared with the $Ti(OR)_{0.5}Cl_{3.5}/MgCl_2$-supported catalyst system.

closely. It is, however, noteworthy that the polymer particles in Figure 3 are 0.1–0.4 μm in diameter, obviously smaller than those in Figures 1 and 2. Furthermore, the large particles over 0.5 μm in diameter could be hardly found in other fields. It is, therefore, most likely that the surface polymer globules observed by SEM are aggregates of some primary polymer particles, probably some tens of primary polymer particles, judging from a difference in size. The aggregates indicated by arrows in Figure 3 seem comparable in size to the surface polymer globules. To examine the polymer particles in more detail, we observed this specimen at a higher magnification. An electron micrograph of sample A is shown in Figure 4, where a number of the 0.2–0.35-μm primary polymer particles can

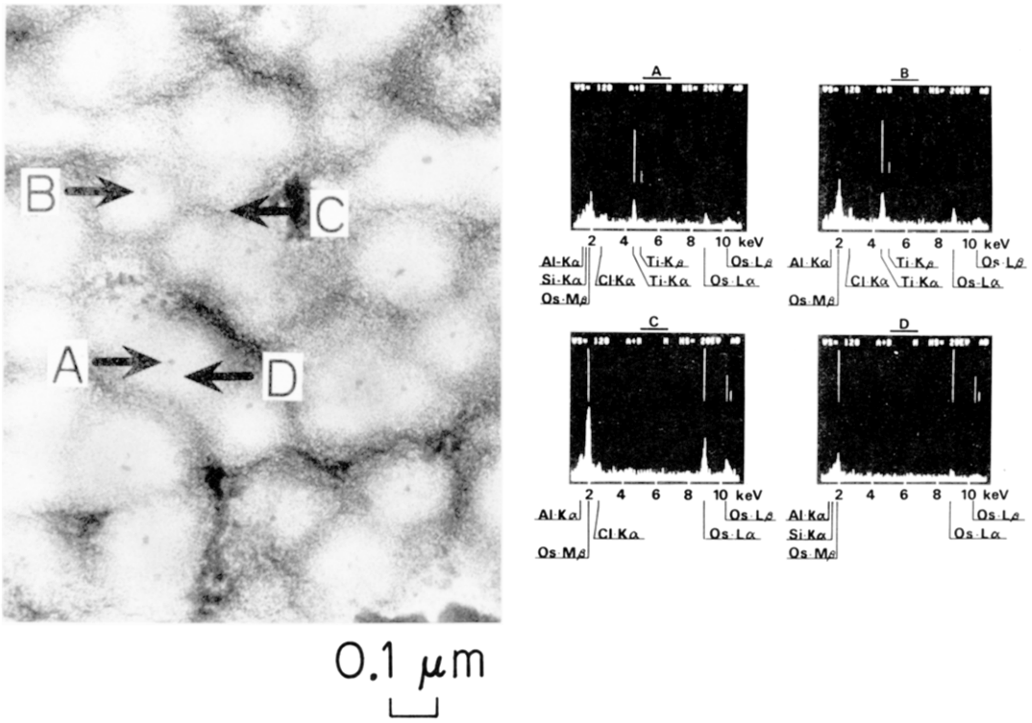

Figure 7. X-ray microanalysis of sample A prepared with the δ-$TiCl_3$ catalyst system.

Table III
Size of Polymer Globules on the Surfaces of Polymer Particles

	size of polym globules, μm	
sample	obsd	calcd[a]
A	1.0	0.27
B	0.9	0.20

[a] See the text. The arithmetic mean of D_{300} and D_{003} was taken as an average size of the catalyst crystallites.

be observed containing one or sometimes two nuclei with diameters of 80–170 Å at the core of each of them. Judging from their size, these nuclei are considered to be the catalyst crystallites. In the case of styrene–butadiene block copolymer, Berney et al.[19] pointed out that the average radius of polybutadiene spheres as determined from the electron micrographs is 23% smaller than the value obtained by small-angle neutron scattering. In this study, however, polypropylene is a crystalline polymer and the inner part of the primary polymer particles is not stained. Therefore, the influence of 1,7-octadiene and OsO_4 on the radius should be small. Even if the radius became smaller to some extent during staining and, therefore, the actual radius is larger by 23%, the polymer globules are 2–4 times larger than the primary polymer particles. As shown in Figures 5 and 6, similar pictures are observed in the polymer particles prepared with the $TiCl_3$AA and supported catalyst systems. The nuclei observed in sample B have diameters of 100–170 Å, and those in sample C have diameters of 50–150 Å. These diameters are also very close to those of the corresponding catalyst crystallites. This indicates that the initial catalyst crystallites may retain their size during the course of polymerization, which is different from the conclusion obtained by Buls and Higgins.[2] In their observation the $TiCl_3$ (AA type) broke up immediately into the basic 100–1000-Å particles, which gradually disappeared and finally dispersed completely in the polymer particles. The polymer yields of the samples examined by them were at most 1900 g of polymer/g of catalyst, which is very close to that of sample B prepared by the $TiCl_3$AA catalyst system. In our observation the primary catalyst crystallites seem to retain at least until this polymer yield, which was confirmed by small-angle X-ray scattering measurement of nascent polypropylene particles.[20] The polymerization activity of the $TiCl_3$ catalyst is known to be highly dependent on the size of the original catalyst crystallite.[13] If the original catalyst crystallite broke down further, such dependence could not be expected to hold. Therefore the present finding seems reasonable. In the case of sample C, polymer particles still contain some catalyst crystallites and the primary polymer particles could not be observed yet at this polymer yield. As a result, the nascent polymer particles are proved to be agglomerates of the primary polymer particles 0.2–0.35 μm in diameter, irrespective of the sorts of catalysts. Next, sample A as the representative sample was examined by X-ray microanalysis. As shown in Figure 7, titanium was detected only from the nuclei represented by A and B and not from any other portions, which proves that the nuclei are the catalyst crystallites.

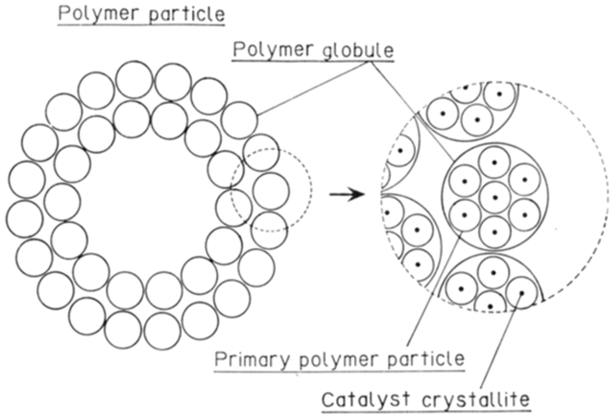

Figure 8. Microstructure of a nascent polymer particle.

From these observation results, we illustrate the microstructure of the nascent polymer particle in Figure 8. The nascent polymer particle is a tertiary particle consisting of secondary polymer globules having diameters of about 1 μm. And the secondary polymer globules consist of some tens of much smaller primary polymer particles 0.2–0.35 μm in diameter, though these diameters may naturally vary, depending on the polymer yield and crystallite size.

At present the reason the secondary polymer globules are formed cannot be elucidated. To make this point clearer, we continue to make some additional studies.

Registry No. OsO_4, 20816-12-0; $MgCl_2$, 7786-30-3; $Al(C_2H_5)_2Cl$, 96-10-6; $Al(C_2H_5)_3$, 97-93-8; $TiCl_3$, 7705-07-9; polypropylene, 9003-07-0; 1,7-octadiene, 3710-30-3; methyl *p*-toluate, 99-75-2.

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Infrared and X-ray Diffraction Studies of a Semirigid Polyurethane

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ABSTRACT: A polyurethane containing a mesogenic diol has been studied by a combination of infrared spectroscopy and X-ray diffraction. Both techniques indicate that this polyurethane develops extremely high order/crystallinity upon annealing. Mid- and far-infrared studies indicate a variety of hydrogen-bonded environments exist in this polyurethane, even in the highly ordered state. In addition to the spectroscopic features arising from intermolecular interactions found for the carbonyl and N–H stretching vibrations, a band sensitive to chain packing and to temperature changes and found at approximately 105 cm^{-1} can be assigned to hydrogen-bonded stretching between the N—H and the C=O groups. Infrared spectra change continuously with increasing temperature. However, only minor changes were observed at isotropization. Considerably different deuterium exchange rates found for urethane hydrogens also suggest different hydrogen bonds in this polyurethane. X-ray studies indicate that the mesophase is of a "cybotactic" nematic type and that the ordered/crystalline state may retain this kind of ordering.

Introduction

Semirigid polymers represent an important and interesting class of materials. A great number of these systems have the potential for strongly ordered structure in the solid state and may have the possibility of exhibiting a liquid crystalline phase. In this study we have given emphasis to a class of semirigid polyurethanes. Unlike many other semirigid polymers, these polymers are strongly interacting. The principal goal in many previous studies has been to obtain a better understanding of the molecular features that allow for the development of the liquid crystalline state. However, most of the studies have concentrated on rigid or semirigid rod systems where the interactions are limited to excluded volume effects and dispersive forces.[1-3] A large body of work exists detailing the effect of specific hydrogen-bonding interactions in polyurethane systems.[4-10] The system examined in this study has been shown to exhibit unique mechanical properties relative to more conventional flexible polyurethanes.[11] We would like to understand how the presence of the rigid regions and the hydrogen-bonding interactions in these polymers affect the ultimate structure and resultant properties.

We have been interested for some time in understanding the nature of phase transitions as they relate to the degree of order and disorder in polymeric systems. The microstructural changes in the various functionalities within a polymer that accompany phase transitions can have varying contributions to the overall process. At least two phase transitions have been observed for these new poly-

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