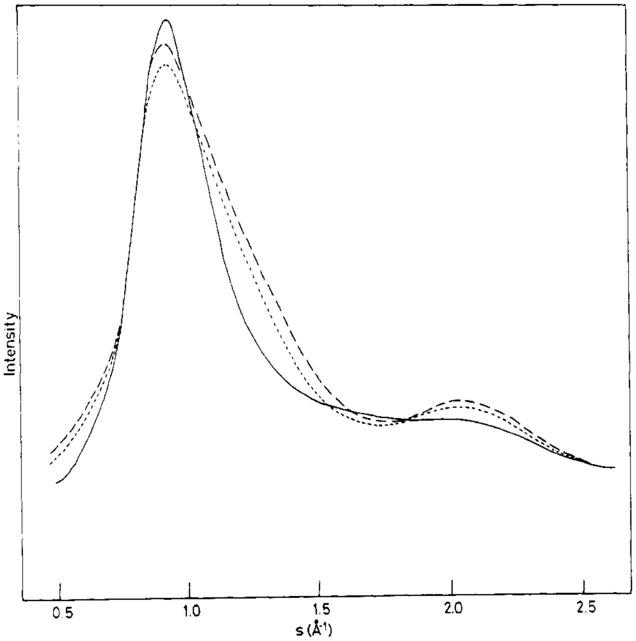

Figure 1. Uncorrected diffracted intensity from (—) quenched i-PMMA, (---) quenched s-PMMA, and (···) a-PMMA. All specimens were unoriented. $s = (4\pi \sin \theta)/\lambda$.

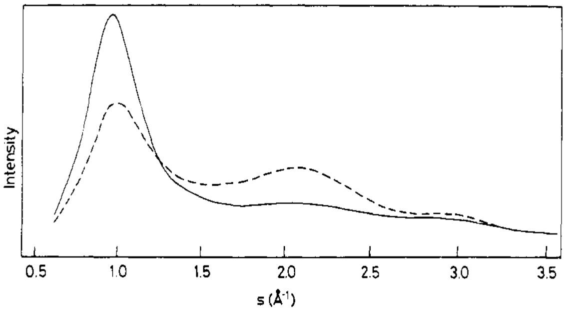

Figure 2. Uncorrected intensity from oriented noncrystalline i-PMMA: (—) equatorial scan; (---) meridional scan.

plastic deformation[12] shows that, although the first peak for a- and s-PMMAs is predominantly equatorial, there is an off-axis component at $s \approx 1.2$ Å^{-1}, which leads to the asymmetry of the peak. For i-PMMA, however, the first peak of the oriented polymer is almost entirely equatorial with no evidence of another component (Figure 2).

The position of the equatorial peak gives a measure of the predominant distance between chains. This distance is most easily determined by transforming suitably corrected scattering data to obtain the radial distribution function (RDF). The sharp equatorial peak in the scattering transforms into a slowly damped oscillation in the RDF.[13] This form of the RDF is generally found for highly disordered structures in which the nearest-neighbor distance is well-defined. Examples of such structures are liquid argon,[14] liquid neopentane,[15] and randomly packed spheres or disks (both real models[16,17] and computer simulations[18,19]).

For a-PMMA, the first broad peak in the RDF has two sharper intrachain peaks superimposed on it.[20] However, a cylindrical distribution function derived from oriented a-PMMA separates these features[21] to show a broad interchain peak centered on 8.2 Å. The similarity in position and peak height of the equatorial scattering from i-PMMA means that the predominant interchain distance is also about 8 Å in the quenched, isotactic polymer. This value is typical for an unpaired PMMA molecule in a near-all-trans conformation, whereas the double helix proposed for the crystalline material has a diameter of at least 12 Å (see Figures 1 and 3 of ref 1). In addition there is no suggestion of a peak in our data near $s = 0.7$ Å^{-1} which would indicate the presence of 12-Å-diameter molecules.

The conclusion is that the molecular diameters for the different isomers of PMMA are similar at around 8 Å. Thus, for quenched or molten i-PMMA, there is no evidence that the molecules are paired as double helices. If double helices are present in the crystal (as has been proposed by Tadokoro and co-workers[1]), then their component molecules would need to pair and regularly intertwine as a part of the crystallization process.

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Orientation Studies of Segmented Polyether Poly(urethaneurea) Elastomers by Infrared Dichroism

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Introduction

Recently we compared the composition–structure–properties of two series of polyether poly(urethaneureas) by various physicochemical techniques and careful me-

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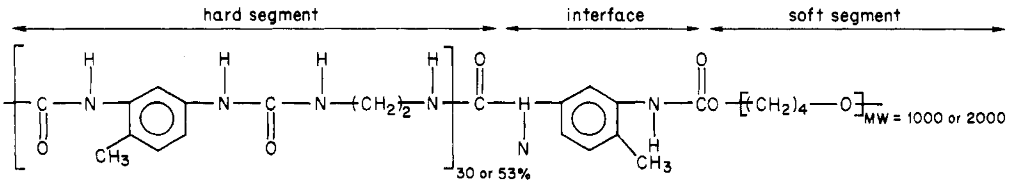

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chanical property measurements.[1,2] These polymers have only amorphous hard-segment domains and an amorphous polyether soft-segment phase. The hard segment in these polymers consists of 2,4-toluene diisocyanate and ethylenediamine, while the soft segment is either 1000 molecular weight (PTMO 1000) or 2000 molecular weight (PTMO 2000). It was reported that both series exhibit extensive phase segregation. But there were indications of subtle differences in morphology between these two series: first, the PTMO 2000 samples have a purer soft-segment phase than the PTMO 1000 samples; secondly, mechanical properties suggest that the hard-segment domain in the PTMO 1000 samples may be more interconnected than that in the PTMO 2000 samples. As a way of providing additional support for the suggested difference in domain morphology between these two series and to shed light on their deformation mechanism, we have carried out orientation studies by transmission IR dichroism, which is a powerful and sensitive technique for understanding morphology and deformation behavior of segmented polyurethanes and poly(urethaneureas) because one can usually assign an appropriate IR band representing the hard-segment domain, soft-segment phase, and the interface between them, assuming that phase segregation is extensive. Cooper and co-workers found that when both the soft and hard segments are amorphous, both segments orient into the stretch direction.[3,4] The extent of orientation depended on the content of hard segment in amorphous polyurethanes, mainly reflecting domain morphology changes from isolated to interconnected domains. With partly crystalline hard segments, their orientation is negative at low elongations but becomes positive at higher elongation. They also observed differences in the orientability of the hard segment when comparing polyurethanes with extensively hydrogen-bonded domains with those without intermolecular hydrogen bonding.[5] Kimura et al. found similar orientation behavior of the hard segment in more crystallizable polyether poly(urethaneureas) which exhibited spherulitic texture.[6]

The morphological models of lamellar domains whose thickness is short as determined by the hard-segment length, but whose long dimension is perpendicular to the hard-segment backbone, have been used to explain this transverse hard-segment orientation, suggesting that the long axis of the lamellar domain was turning into the stretch direction at low elongations.[4,6] More recently, with a polyether poly(urethaneurea) (composed of 2,4-TDI, 4,4′-diaminodiphenylmethane, and PTMO), Khransovskii offered a somewhat different interpretation for the observed transverse orientation at low elongations: that of the conformational transition from the twisted form of the hard segment to the more extended conformations.[7] In his polymer, the hard segment, most likely amorphous, contains a great deal of aromatic benzene rings connected with urea linkage, which can lead into the twisted form due to steric hindrance.

In summary, results obtained by previous IR dichroism studies have shown that the composition, intermolecular bonding, and morphology of polyurethanes and poly(urethaneureas), especially in the hard segment, strongly affect their orientation behavior.

Table I
Composition and Properties of Polyether Poly(urethaneureas)

molar composition	overall urea content, %	T_{g_1},[a] °C	T_{g_2},[b] °C	ultimate tensile strength, kg/cm^2	% hysteresis at 50% strain
	2,4-TDI-ED-PTMO 1000				
2:1:1	30	−53	192	400	72
5:4:1	53	−53	180	600	77
	2,4-TDI-ED-PTMO 2000				
4:3:1	30	−74	190	250	35

[a] T_{g_1} = glass transition of the soft-segment phase. [b] T_{g_2} = glass transition of the hard-segment domain.

Experimental Section

Materials. The syntheses of polyether poly(urethaneureas) was described in an earlier paper.[1] The chemical structure of the polyether poly(urethaneureas) studied is shown in I. Table I summarizes the composition and properties of the three polymers used in this orientation study.

Sample Preparation. Thin films were cast from dimethylformamide solution onto a clean glass, followed by drying in a vacuum oven at 50 °C for at least 2 days to completely remove the solvent.

IR Dichroic Studies. A Fourier transform IR spectrometer (FTS-14) from Digilab was used with a Brewster's angle crossed plate polarizer, germanium double-diamond polarizer (PDD-01B) from Harrick Scientific Corp, which was chosen over the wire grid type polarizer because of its greater transmission intensity (over 50%) at similar polarization efficiency (99%).

Sample films were placed before the polarizer in the sample compartment in a small stretching jig. After each extension and allowing the sample to reach constant orientation, the IR spectra after 100 scans from the center part of the film were recorded both for parallel and perpendicular polarizations. Instrument polarization effect was estimated by measuring the polarizer transmission curve as a function of polarizer angle and found to be relatively small. Nevertheless necessary corrections were made when calculating the dichroic ratio. Data were analyzed first by calculating the dichroic ratio D ($A_\parallel / A_\perp$) from the recorded spectra and relating to an orientation function f by the equation

$$f = \frac{D_0 + 2}{D_0 - 1} \frac{D - 1}{D + 2}$$

where D_0 is the dichroic ratio for perfect alignment of the polymer chains with the stretch direction and is equal to $2 \cot^2 \alpha$, α being the angle between the transition moment vector for the vibration and the local chain axis. For the hard-segment orientation, the NH band at 3330 cm^{-1} was used rather than urea carbonyl because of the difficulty of deconvoluting the latter from the overlapping peaks. Asymmetric CH$_2$ vibration at 2960 cm^{-1} was used for the soft segment. Our previous studies[2] indicated that much of the urethane carbonyl which is present at the interface between the hard-segment domain and the soft-segment phase is free of hydrogen bonding, suggesting a fairly sharp interface. Careful small-angle X-ray scattering studies support this suggestion.[8] Therefore, free urethane carbonyl at 1740 cm^{-1} was taken to represent the interface between the hard-segment domain and

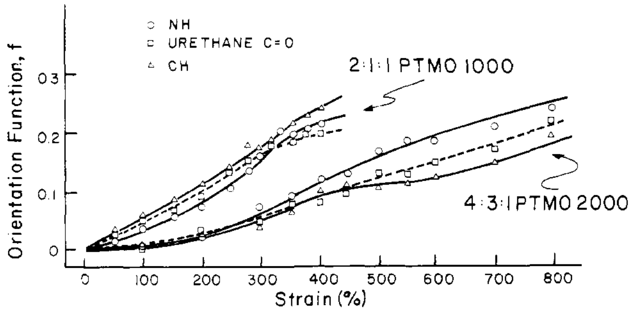

Figure 1. Orientation function vs. strain for 2:1:1 PTMO 1000 and 4:3:1 PTMO 2000.

the soft segment. For NH and CH_2, a transition moment direction of 90° was assumed, while 79° was used for the urethane carbonyl.[4]

Results and Discussion

In our samples, at least in the undeformed state, no crystallinity was observed either in the hard-segment domain or in the soft-segment phase, as evidenced by both wide-angle X-ray diffraction and DSC studies. The results obtained in this study are based on extending one sample uniaxially by step increments and scanning the polarized IR spectra at each step, with the sample under tension. Dichroic studies after cyclic strain were not carried out.

The upper curves in Figure 1 show the orientation functions vs. strain for a 2:1:1 sample of the PTMO 1000 series which has a 30% overall urea content. It is noted that the orientation of the hard segment, soft segment, and interface is of similar magnitude and is always positive, meaning that the orientation occurs parallel to the stretch direction at all elongations. Orientation functions for all bands studied here reach about 0.25 at 400% strain. It may appear rather surprising that both the flexible soft segment and the stiffer hard segment reach similar values of orientation. This may be in part due to the particular morphology of this sample, but it may also be related to the manner in which the experiment is carried out, recording the spectra with the sample under tension. Estes et al. found similar results upon initial strain on some MDI-based polyurethanes but found that residual orientation following a 5-min relaxation period at zero load was much greater for the hard segment than for the soft segment.[3] For a 5:4:1 sample of the same PTMO 1000 series which has a 53% urea content, orientation behavior and magnitude are very similar to those for the 2:1:1 sample. Therefore it can be concluded that the morphology and the deformation mechanism in the PTMO 1000 series between 30 and 53% urea content are quite similar. On the other hand, the extent of orientation of the PTMO 2000 sample at 30% urea content (4:3:1 sample) is found to be significantly lower, as shown in the lower curves in Figure 1.

Our results clearly indicate that the major difference between the PTMO 1000 series and the PTMO 2000 series is higher orientation for the former than for the latter. This difference is similar to the change observed by Seymour et al. when the MDI content in their MDI–BD (butanediol)–PTMO 1000 series was increased from 24 to 28% and greater, which was interpreted as due to the morphology changes to interconnected domains at higher MDI content.[4] By the same analogy, our results suggest greater interconnectivity in the PTMO 1000 sample as compared to the PTMO 2000 sample. It is noted that our proposed model is consistent with the suggestion we made earlier based on mechanical properties, especially a comparison of hysteresis measurement and ultimate tensile strength between these two series.[2] (The PTMO 2000 samples exhibited lower hysteresis and ultimate tensile strength than the PTMO 1000 samples, as summarized in Table I.)

IR dichroism studies seem to offer some opportunities to probe the strength of intermolecular hydrogen bonding in the hard-segment domains. For example, in piperazine-based polyurethanes which lack such bonding in the hard segment, Allegrezza et al. have observed a higher degree of hard-segment orientation (orientation function between 0.6 and 0.8 at 250% strain) than in MDI-based polyurethanes, and they interpreted this as due to the breakdown of the original spherulitic texture facilitated by the lack of intermolecular hydrogen bonding in the hard segment.[5] In light of this, we have compared our orientation values with those obtained by Seymour et al.[4] on amorphous MDI-based polymers which have a similar morphology to ours. For example, comparison of our 2:1:1 sample (PTMO 1000 series) with their polyurethane which has about 33% urethane content (28% MDI content) indicates that the orientation of the soft segment is comparable while the orientation of the hard segment in our sample is much lower than in their sample. Specifically, in our sample an orientation function of about 0.1 is attained as compared to 0.4 for their sample at 250% strain. By an analogy similar to that used in the comparison between piperazine-based and MDI-based polyurethanes, the lower level of hard-segment orientation in our polymers seems to indicate stronger intermolecular hydrogen bonding in the domains as compared to MDI-based polymers. Both in our samples and in Seymour's MDI-based polyurethanes, extensive intermolecular hydrogen bonding was observed in the hard-segment domains. However, there could be some subtle differences between polyurethanes and poly(urethaneureas) which can bring about stronger intermolecular bonding in the latter. For example, in our earlier studies,[2] we suggested the presence of three-dimensional hydrogen bonding in the hard-segment domains, where one urea carbonyl is bonded to two NH groups belonging to other chains, in our poly(urethaneureas) (extended with diamine), but not in polyurethanes (extended with diol). The indication of the stronger interdomain bonding implied by this study is not in conflict with the presence of such a type of hydrogen bond in our poly(urethaneurea) domains.

It would have been interesting to compare our polymers with polyurethanes based on the same diisocyanate, 2,4-TDI. However, polyurethanes based on 2,4-TDI–BD (butanediol)–PTMO 1000 at the same hard-segment content (about 30%) exhibited very poor phase segregation,[9] which makes it difficult for the proper IR band assignment to represent each phase. This has prevented a direct comparison.

Quantitative small-angle X-ray scattering studies carried out recently on these samples lend further support to all the arguments put forth in this paper. A full paper on SAXS results is in preparation.

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Distinction between Hexyl and Longer Branches in Polyethylene by 67.9-MHz Carbon-13 Nuclear Magnetic Resonance

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Almost all papers concerning the analysis of branched polyethylene by ^{13}C NMR[1-5] repeat in some way the statement of Randall[1] that branches of lengths of 1–5 carbon atoms can be mutually distinguished but that at a branch length of six carbon atoms the array of chemical shifts associated with branch length may no longer change with increasing chain length. Only in one instance[2] has it been claimed that amyl branches could not be recognized separately from ethyl, propyl, butyl, and higher branches, but the feasibility of this distinction has again been demonstrated by Randall.[3]

In his early work,[1] Randall performed a 25.2-MHz analysis of ethylene copolymers with olefins ranging from propene to octene. For the heptene copolymer, he found that the resonances of the carbons C-4 and C-β[7] ($\Delta\delta = 0.57$ ppm) could be easily resolved, while those of C-5 and C-α could hardly be resolved with the experimental techniques applied at that time. In the octene copolymer, C-5 and C-6 are equivalent to C-4 and C-5 in the heptene copolymer with respect to their distance from the branching point. No difference between the chemical shifts of C-5 and C-β on the one hand and C-6 and C-α on the other hand was detected by Randall for the octene copolymer.

In a more recent work, Axelson, Levy, and Mandelkern[5] again conclude that "long branches cannot be distinguished from hexyl at the present time". Furthermore, they state that "while high magnetic fields lead to a greater dispersion of chemical shifts, we have found that a comparison of spectra obtained at 67.9 MHz with that at 22.6 MHz does not reveal significant changes in the information content".

This is not entirely true, at least regarding the distinction between hexyl and longer branches. In our view, the ability to resolve the resonances of C-5 and C-β in polymers bearing the hexyl group is crucial to this distinction. Other branch carbon resonances are not suited to this purpose. C-6 is too far away from the branch end to reflect the effects of its increasing length; C-4 and C-(4 + n) in branches of length (6 + n) will be obscured by the resonance of unperturbed main-chain methylene carbons; other branch carbons will behave like C-4 or will be indistinguishable from terminal main-chain carbons.

We performed a comparative analysis at 25.2 and 67.9 MHz of two octene copolymers. One was a commercial linear low-density polyethylene sample, Dow 61500.49; the other was prepared in our laboratories. The 67.9-MHz carbon-13 spectrum of the latter is shown in Figure 1.

In both cases, we were able to resolve the C-5 and C-β resonances at 67.9 MHz, their separation amounting to 0.027 ppm (1.8 Hz); the less intense high-field resonance is assigned to C-5. The chemical shifts of all carbon nuclei detected at 67.9 MHz are summarized in Table I.

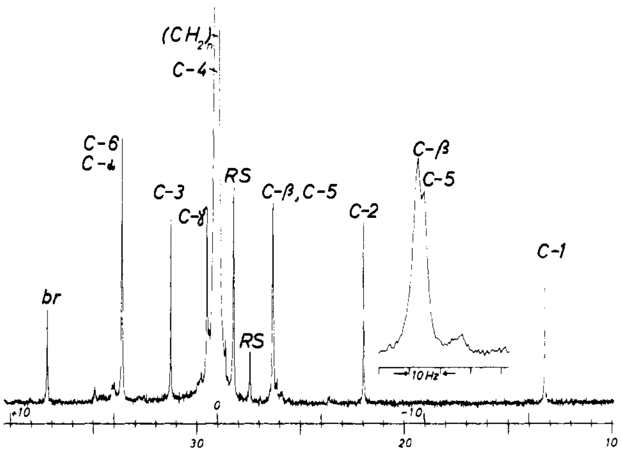

Figure 1. 67.9-MHz ^{13}C NMR spectrum of an ethylene–octene copolymer. RS = rotational sideband.

Table I
Carbon-13 Chemical Shifts (ppm) in the Ethylene-Octene Copolymer

carbon	shift[a]	shift[b]
branch	37.214	8.198
C-α, C-6	33.610	4.593
C-3	31.273	2.225
C-γ	29.502	0.485
C-4	obscured by (CH$_2$)$_n$	
(CH$_2$)$_n$	29.016	0.000
C-β	26.329	−2.688
C-5	26.302	−2.715
C-2	21.960	−7.056
C-1	13.250	−15.767

[a] Referenced to the resonance of internal octamethylcyclotetrasiloxane. [b] Referenced to the main methylene resonance.

On the contrary, the 25.2-MHz spectra showed no resolution at all between the resonances of C-β and C-5.

We therefore conclude that—at least for the purpose of identification of ethylene–1-olefin copolymers—hexyl can be distinguished from longer branches at 67.9 MHz by looking at the resonance at 26.3 ppm (internal octamethylcyclotetrasiloxane reference) or at −2.7 ppm (main methylene peak reference). A careful choice of experimental conditions (see Experimental Section) is, however, necessary.

We wonder if at the higher fields now available (carbon-13 resonance up to 125 MHz) it will be possible to elaborate specific assignments for carbons of even longer branches. Both the increase in the dispersion of the chemical shifts and in the sensitivity, which may allow the application of modern resolution enhancement techniques, should make it worthwhile to try.

Experimental Section

The 67.9-MHz carbon-13 spectra were obtained at 120 °C with a Bruker HX-270 spectrometer operating in the quadrature detection mode and equipped with a Bruker Aspect 2000 computer; for the 25.2-MHz spectra, a Varian XL-100/15 spectrometer equipped with a Varian 620 L computer and an interactive disk unit was used. Sample concentration was 40% (w/v) in a solvent mixture made up to 65% hexachlorobutadiene and 35% (v/v) 1,1-dideuteriotetrachloroethane, which has a high boiling point and displays good solvent properties for polyethylene; moreover, it provides the internal lock which is an essential requisite for good spectral resolution. Internal tetrachloroethane should therefore be preferred to internal perdeuteriobenzene or to any

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