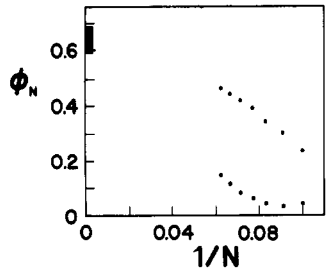

Figure 8. Effective ϕ estimates vs. $1/N$, for the TR lattice ($10 \le N \le 16$). The upper (lower) values correspond to the rightmost (next-to-rightmost) zeros. The range of eq 7 is marked on the ϕ axis.

imaginary part (eq 6), we plotted in Figure 8, the effective ϕ estimates

$$\phi_N = \ln (y_N/y_{N-1})/\ln [(N-1)/N] \qquad (8)$$

vs. $1/N$, for the TR lattice. The values for $N \le 16$ are below 0.64, but their trend in Figure 8 is consistent with them extrapolating toward the range of eq 7 as $N \to \infty$. Study of the SQ-lattice data with $N - 1$ replaced by $N - 2$ in eq 8 produced irregular sequences (all $\phi_N < 0.64$ for $N \le 21$) which, however, show an upward trend similar to the TR-lattice results.

Having an *infinite-slope* locus is not inconsistent with the trend in Figures 4 and 5. By the general considerations of ref 28, the 90° angle implies equal specific heat divergence amplitudes below and above the ϵ_t. The available data, however, are not sufficient to conclusively substantiate this possibility.

In summary, our study of the partition function zeros in the $d = 2$ Θ-point lattice model provides a convincing indication of the existence of a unique transition point at the location consistent with that found in other, "real-axis" numerical studies.

Acknowledgment. We acknowledge instructive discussions with Professor L. S. Schulman.

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^{13}C CP/MAS NMR Study of the Polypivalolactone Polymorphs

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ABSTRACT: High-resolution ^{13}C CP/MAS NMR spectra have been obtained for the α, β, and γ polymorphs of polypivalolactone, providing information on their molecular conformation in the solid state. The ^{13}C CP/MAS NMR spectra of the α and γ forms are identical, suggesting that these forms have the same molecular conformation. A characteristic 1:1 doublet is observed for the two chemically "equivalent" methyl carbons, in agreement with the well-established 2_1-helical conformation of the polymer chain in the α form. In contrast, the ^{13}C CP/MAS NMR spectrum of the β form is different from that of the α and γ forms and shows a single peak for the two methyl carbons. The spectrum of the β form is consistent with a planar zigzag molecular conformation for this polymorph.

Introduction

Polypivalolactone (PPL) is the prototype in the series of synthetic α,α-disubstituted polyesters with the general formula

$$-(CH_2CR_1R_2COO)_n- \quad \mathbf{1}$$

where R_1 and R_2 represent various aliphatic substituents. The initial synthesis of these materials by Thiebaut and co-workers,[1] using a range of R_1 and R_2 substituents (both symmetric and asymmetric) produced non-optically active but crystalline polymers. The effect of chirality on melting points was investigated by Grenier et al.,[2] who synthesized poly(α-methyl-α-ethyl-β-propiolactone) of different enantiomeric compositions and oberved a large increase in melting point for the optically pure polymer. The symmetrically substituted polymers are the most crystalline and show the highest melting points (around 230–240 °C), as in PPL where $R_1 = R_2 = CH_3$. As the asymmetry in size of the R_1 and R_2 substituents increases, the melting points decrease in a regular fashion, and the mechanical properties at room temperature approach those of a "soft" elastomer.[1,3] All evidence suggests that the optically active polymers rather than the racemic products would lead to more ordered structures with higher melting points.[2,4]

It is generally accepted that all the polyesters based on the above structure crystallize with a regular 2_1-helical conformation of the polymer chain,[4] as in the case of the chiral poly(β-hydroxybutyrate).[5] In particular, the X-ray analysis of crystalline polypivalolactone fibers is on a good foundation.[6,7] These PPL fibers were considered for textile applications;[8] however, under stress they exhibit a cold-flow property, which is considered a serious shortcoming. The cold flow is associated with the formation of a metastable β-crystalline form, wherein the 2_1-helical chains of the α form are drawn into a planar zigzag arrangement.[8,9] Conformational calculations have shown that the 2_1 form corresponds to the global energy minimum in the conformational map.[4,10] Besides the α-to-β polymorphic transformation (which resembles the helix-to-planar chain transition in proteins), a third polymorph of PPL called the γ form has been reported.[11,12] Electron diffraction evidence suggests that this form has the same chain conformation as the α form.[12]

The recently developed techniques of ^{13}C cross polarization and magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy yield high-resolution NMR spectra in the solid state.[13] The chemical shifts obtained in these spectra are the "isotropic" values for the solid state. These shifts are thus similar in nature to those obtained in solution and may be used for structural elucidation in terms of both molecular and crystal structures. Although the ^{13}C CP/MAS spectra of solids yield isotropic shifts as in the solution, the solid-state spectra can be more complex due to inequivalencies that may be induced between "equivalent" nuclei by the solid state. The interpretation of those complex spectra, especially in conjunction with X-ray diffraction data, has yielded much information on the crystalline structure of both natural and synthetic polymers as shown by recent work on cellulose,[14] starch,[15] and polypropylene.[16] In addition, the line widths observed in ^{13}C CP/MAS spectra are dependent on the short-range order about the carbon atom observed.

Since detailed fiber diffraction data are presently lacking for both the β and γ forms of PPL, the present study was undertaken to allow comparison of the solid-state structures of the three polymorphs of PPL, using ^{13}C CP/MAS NMR.

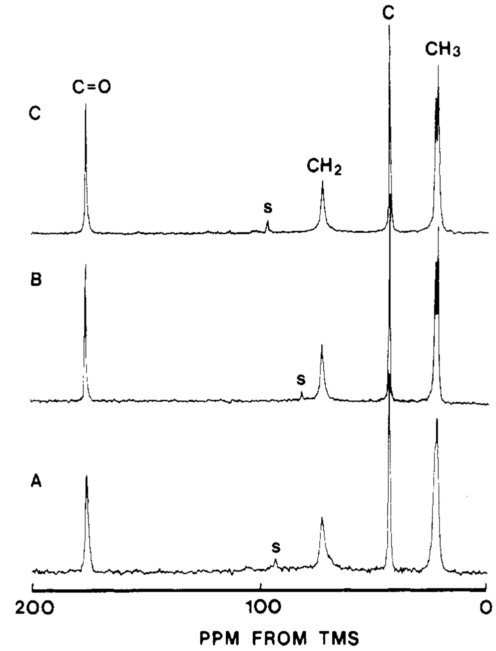

Figure 1. ^{13}C CP/MAS NMR spectra of solid polypivalolactone: (A) untreated PPL fibers (α form); (B) annealed PPL beads (α form); (C) PPL beads quenched from the melt (mixture of α and γ forms). All spectra are the accumulation of approximately 15000 acquisitions, with a 1-ms contact time and a 1-s delay time. The spectra are plotted without line broadening. Peaks denoted by an "s" are spinning sidebands from the carbonyl resonance.

Table I
^{13}C Solid-State Chemical Shifts of Polypivalolactone Polymorphs[a]

	CH_3	-C-	CH_2	C=O
α form	22.4, 23.5	43.6	73.3	176.0
β form	22.8	43.1	71.8	175.0
γ form	22.4, 23.5	43.6	73.3	176.0

[a] Shifts in ppm relative to Me_4Si, and the precision of the shifts is estimated to be ±0.4 ppm (95% confidence level).

Experimental Section

Oriented melt-spun PPL fibers were obtained as fibers from Dr. F. L. Binsbergen of the Koninklijke/Shell Laboratorium in Amsterdam (this sample has been characterized in ref 9 and 17) or as beads from Polysciences. Stretched PPL fibers were obtained by stretching fiber bundles to the break at room temperature. Annealing was typically done at 180 °C for 2–4 h, followed by slow cooling to room temperature. Samples rich in the γ form were prepared by melting PPL beads at 260 °C (T_m for the form is 240 °C) in a glass dish on a hot plate, followed by quenching at room temperature by removing the dish and placing it on the bench top.

Powder X-ray diffraction patterns were obtained with a Rigaku diffractometer with nickel-filtered Cu Kα radiation (λ = 1.542 Å).

The ^{13}C CP/MAS NMR solid-state spectra were obtained with a commercial Bruker CXP-100 with an iron magnet operating at 22.6 MHz and a home-built MAS probe. A decoupling field of 12 Gauss and spinning rates of ~2.5 kHz were used. ^{13}C CP/MAS spectra were obtained with a 1-ms contact time and a 1-s recycle delay. The magic angle was set by adding 50 mg of KBr or NaBr to each sample using the method of Frye and Maciel[18] and observing the ^{79}Br resonance. The spectra were referenced to external hexamethyldisiloxane (by substitution), and the shifts were converted to Me_4Si by adding 2.1 ppm to the measured shifts.

Results and Discussion

The ^{13}C CP/MAS NMR spectra of PPL beads and fibers, after various sample treatments, are shown in Figures 1 and 2. The ^{13}C solid-state chemical shifts are listed in Table I. The PPL polymorphs present in each sample were determined by X-ray powder diffraction, which shows characteristic patterns for the α, β, and γ structures.[9,11] The α and γ forms were identified by their characteristic *d* spacings shown in Table II.[11] The β form can be identified by the increase in intensity of the 4.94-Å reflection relative to the α- and γ-form reflections.[9]

Table II
d Spacings for the Polypivalolactone Polymorphs[a]

annealed fiber	α form[b]	stretched fiber[c]	β form[d]	quenched beads[e]	γ form[f]
7.56	7.77	7.75		7.65	
5.75	5.80	5.80		6.70	6.67
5.25	5.16	4.94	4.94	5.75	
4.96	4.94		4.76	5.63	5.61
4.15	4.16			4.95	4.94
3.83	3.84			4.46	4.48
3.55	3.55			4.15	
3.10	3.13			4.07	4.08
3.00	3.00			4.00	3.99
2.89				3.83	
2.60	2.57			3.55	
2.47	2.49			3.14	3.16
2.37				3.10	
2.16				3.00	2.98
2.10				2.89	
2.07				2.60	
				2.47	
				2.37	

[a] All *d* spacings in Å. [b] From ref 11. [c] The 4.76-Å reflection is not observed due to overlap with the very strong 4.94-Å reflection. The reflections at 7.75 and 5.50 Å are due to the presence of the α form in this sample. [d] From ref 9. [e] Reflections not assigned to the γ form are due to the presence of the α form in this sample. [f] From ref 11.

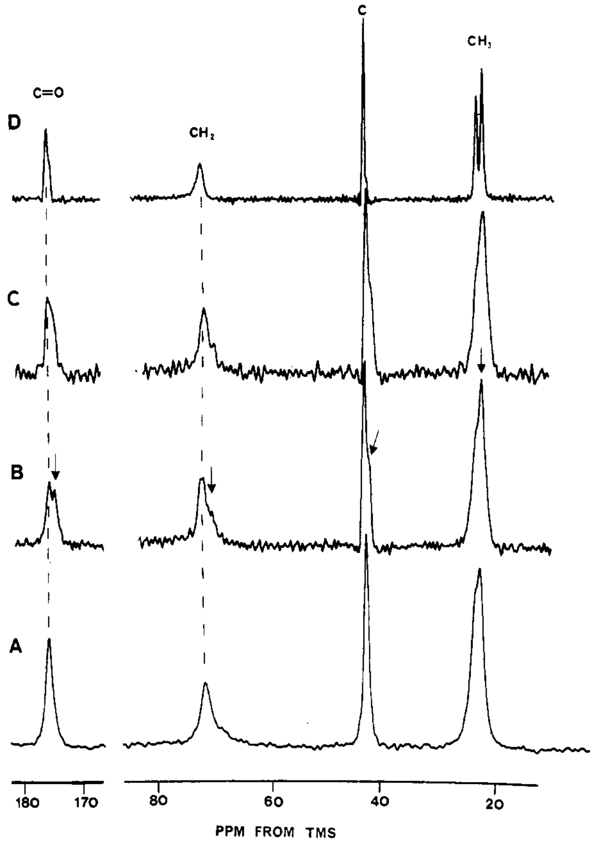

Figure 2. ^{13}C CP/MAS NMR spectra of PPL fibers: (A) untreated fibers (α form); (B) stretched fibers (mixture of α and β forms); (C) stretched fibers, allowed to stand 1 week with no tension (mixture of α and β forms); (D) stretched, then annealed fibers (α form). All spectra were the accumulation of approximately 15 000 acquisitions, with a 1-ms contact time and a 1-s delay time. The spectra were all plotted with −20-Hz Gaussian resolution enhancement. Arrows denote the presence of peaks assigned to resonances arising from the β polymorph.

As expected, the annealed PPL fibers (see Table II) and the untreated PPL fibers shows only the α polymorphic form.[9] However, there is a dramatic increase in the sharpness of the X-ray reflections on annealing of the fibers. This behavior is well documented and reflects an increase in long-range order on annealing. The ^{13}C CP/MAS spectra of PPL fibers also show a very dramatic sharpening of the resonances as a result of the annealing process, as shown in Figures 1 and 2. This similar behavior of the NMR spectra and X-ray patterns suggests the narrowing of the ^{13}C resonances on annealing is associated with an increase of local short-range ordering, concurrent with longer range effects producing crystalline material as reflected by diffraction data. Concomitant narrowing of ^{13}C CP/MAS NMR peaks and X-ray diffraction peaks has been previously observed on hydration of solid β-1,3-D-glucans[19] and starches.[15]

The most obvious interpretation of these results is that the ^{13}C line widths are dependent on the short-range order about the observed carbon atom. In general, the sharpest resonances are observed from carbon atoms in highly ordered environments due to the narrow distribution of chemical shifts. In poorly ordered systems, carbon atoms will have a distribution of local molecular environments, and thus a distribution of chemical shifts giving rise to broader resonances. For example, in solid polyethylene there are two peaks in the ^{13}C NMR spectrum, one arising from the crystalline regions of the polymer, and the other from the noncrystalline regions.[20] In that study, the contributions to the observed line widths for these resonances were estimated. The contribution due to the distribution of chemical shifts was small for the resonance from the crystalline material, giving rise to a very narrow peak, and much larger for the resonance of the noncrystalline material giving a much broader peak. Thus, the very sharp peaks observed for the annealed samples are attributed to the narrow distribution of chemical shifts in the highly ordered crystalline environment of these samples. The NMR spectrum of the untreated fibers shows broader resonances due to the distribution of chemical shifts in the less ordered environment of the untreated fiber. These results are not surprising, in that the "as-received" fibers are the result of a spinning and stretching protocol which optimizes certain physical properties of the fiber, but not the degree of crystalline order, which is optimized by annealing.

Note that there is no evidence of resonances that can be assigned to noncrystalline material, consistent with the high crystallinity of even the "as-received" fibers.[9]

The ^{13}C CP/MAS NMR resonances of PPL can be easily assigned based on the expected ^{13}C shifts in solution, as shown in Figures 1 and 2 and Table I. The ^{13}C CP/MAS spectra of the annealed samples, consisting solely of the α form, show a separate peak for each carbon in the PPL repeat unit. In particular, the spectra show a characteristic doublet for the methyl carbon resonance, although the two methyl carbons in the PPL repeat unit are chemically equivalent. Although the line widths and intensities of these two peaks are slightly different, the ratio of peak areas is 1:1 to this doublet (under the conditions used in this study the NMR peak areas are expected to be quantitative[21]), suggesting that there are two equally populated environments for the methyl carbons. The obvious explanation is that in the solid state there is a fixed conformation of the polymer backbone, which places the two methyl groups of the PPL repeat unit in different environments. The X-ray-determined structure of the α form of PPL consists of two antiparallel, but equivalent chains in the unit cell.[6,7] Each chain adopts a 2_1-helical conformation as shown in Figure 3. The Newman projections in this figure demonstrate clearly that this 2_1-helical conformation results in a different environment for each of

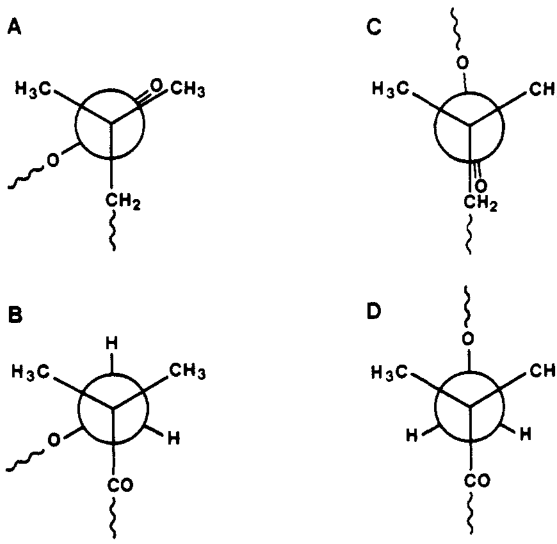

Figure 3. Newman projections for the two conformations of polypivalolactone (A) 2_1-helical conformation, observing down the $-C(CH_3)_2-CO_2-$ bond; (B) 2_1-helical conformation, observing down the $-C(CH_3)_2-CH_2-$ bond; (C) planar zigzag (all trans) conformation, observing down the $-(CH_3)_2-CO_2-$ bond; (D) planar zigzag (all trans) conformation, observing down the $-C(CH_3)_2-CH_2-$ bond.

the two methyl carbons. Thus, two peaks would be expected in the ^{13}C NMR spectrum of the α form as is observed for the annealed samples in Figures 1 and 2. This doublet structure is not well-defined in the spectrum of the untreated fiber (also predominantly in the α form) due to the broadness of the resonance in this less ordered sample, although an incipient splitting of the resonance can be noted.

The ^{13}C CP/MAS NMR spectrum of a sample of PPL quenched from the melt is shown in Figure 1. This sample is a mixture of the α and γ forms of PPL, as shown by the *d* spacings calculated from the X-ray fiber diffraction data (see Table II). As shown by Figure 1, the ^{13}C CP/MAS NMR spectrum of the mixture of α and γ forms is identical with that of the pure α form. Since the α and γ forms of PPL appear to give identical NMR spectra, the local environments of the carbon nuclei in the α- and γ-form crystallites must be very similar. Thus, the γ form crystallizes in a conformation very similar to the 2_1-helical conformation found in the α form. Although no detailed structure of the γ form has been published, a single-crystal electron diffraction analysis has recently suggested that the γ structure is indeed very similar to the α structure.[12] In that work, the γ form is suggested to have a 2_1-helical conformation of 6.04-Å repeat (the repeat is 6.03 Å for the 2_1 helix of the α form), with two antiparallel chains in the unit cell (as in the α form), and similar *a* and *b* lattice parameters to those of the α form. The essential difference is that the γ form was indexed as an orthorhombic unit cell, while the α form has a monoclinic cell. The similarity of the ^{13}C NMR spectra of the α and γ forms thus appears to reflect the similar conformation of the polymer chains in these two structures. However, the NMR spectrum does not appear to be sensitive to the different chain packing in the two unit cells.

The ^{13}C CP/MAS spectrum of a stretched PPL fiber is shown in Figure 2. Stretching of PPL fibers has been shown to induce the β form of PPL. Prud'homme and Marchessault[9] have used the change in intensity of the 4.94-Å reflection from the X-ray powder diffraction data to *arbitrarily* define the amount of α form that has been converted to the β form. Using this method, one finds the amount of β form induced by stretching is 30% in this sample. Comparing the ^{13}C CP/MAS NMR spectra of the stretched fibers to that of the untreated fibers in Figure 2, one additional peak for each of the carbonyl, methylene, quaternary, and methyl carbon resonances appears, although only for the carbonyl and methylene resonances are these peaks well resolved. These four additional peaks can thus be assigned to the β form of PPL, as shown in Figure 2 and Table I.

No detailed structure of the β form of PPL has been published; however, the X-ray fiber diffraction data for the β form show a meridional 4.76-Å reflection, which is consistent with a planar zigzag conformation of the polymer chain. As shown in Figure 3, the two methyl carbons would be equivalent in the planar zigzag conformation of the polymer chain, in contrast to the helical conformation. The ^{13}C NMR spectrum of the β form would thus be expected to show only four peaks: one for each of the carbonyl, methylene, quaternary, and methyl carbon resonances, as is observed.

If, after stretching, the PPL fibers are left for 1 week with no tension, then the four additional resonances assigned to the β form decrease in intensity, as shown in Figure 2. The decrease in the amount of the β form shows the relaxation of PPL fibers from their stretched state, as has been previously noted in X-ray diffraction studies.[9] For a more complete analysis of the β form, one needs a method for preparing a sample which is entirely of the β form as in the case of γ-irradiation of β-propiolactone single crystals.[22]

Conclusions

Symmetry and conformational features are important pieces of information derived from X-ray diffraction analysis of solids. For polymers, the conformational aspects usually require comparison of observed and calculated intensities from both fiber diffraction and single-crystal electron diffraction data, as well as a modeling analysis with energy minimization. For the β and γ forms of PPL, this has not been possible so far. However, the ^{13}C CP/MAS NMR spectra show that the α and γ forms probably have the same molecular conformation. Both forms yield identical spectra, showing a characteristic 1:1 doublet for the two chemically equivalent methyl carbons. These spectra are in agreement with the well-established structure of the α form, which has a 2_1-helical conformation of the polymer chain. In contrast, the ^{13}C CP/MAS NMR spectra show that the molecular conformation of the β form is different from that of the α and γ forms. The spectrum of the former shows only a single line for the two methyl carbons. The spectra observed for the β form are consistent with a planar zigzag molecular conformation for this polymorph.

The inequivalencies between "equivalent" nuclei in the solid-state ^{13}C CP/MAS spectra of polymers may be induced by either a fixed molecular conformation within a polymer chain or the packing of the polymer chains within the unit cell. For the α and γ PPL, the ^{13}C chemical shifts of the methyl carbons are sensitive to the conformation of the polymer backbone within a single monomer unit in a single chain and the shifts of all resonances are insensitive to the different packing of the chains in the two forms. This is an interesting contrast to isotactic polypropylene,[16b] where the ^{13}C chemical shifts of all carbons are sensitive to the intermolecular packing of the polymer chains, giving rise to an inequivalence of chemically "equivalent" carbons. These results highlight the difficulty in interpretation of the complex ^{13}C CP/MAS NMR spectra of such polymers as cellulose[14] and starch,[15] where

X-ray data are ambiguous, in terms of some molecular conformation and intermolecular packing features.

Acknowledgment. We acknowledge the financial assistance of NSERC (Canada) in the form of an operating grant (C.A.F.) and a Graduate Scholarship (R.P.V.). We also acknowledge the technical assistance of C. Pasztor of the University of Guelph and Dr. T. L. Bluhm of the Xerox Research Centre of Canada in obtaining the X-ray diffraction data.

Registry No. PPL (homopolymer), 24969-13-9; PPL (SRU), 24937-51-7.

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Methods for Determining the Molecular Weight and Solution Properties of Polyurethane Block Copolymers

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Received March 21, 1986

ABSTRACT: Molecular weight measurements of polyurethane block copolymers have been made with a GPC–multidetector method and compared to values obtained by the conventional polystyrene standard method and a broad molecular weight distribution calibration standard technique. The multidetector method proposed in this paper produces more accurate molecular weight values and thus its use should allow for better understanding of molecular weight effects on the structure–property relationships of polyurethane block copolymers. The multidetector technique can also be used to obtain Mark–Houwink constants and the distribution of average segmental composition with molecular weight. Mark–Houwink parameters obtained with the multidetector method appear to be more accurate than values calculated with an approach based on broad molecular weight distribution calibration standards and suggest that for a series of polyether polyurethanes in THF, the solvent power decreases with increasing hard-segment content. A comparison of the molecular weight values obtained with the various methods indicates that the relative $\bar{M}_w$ values normally reported based on a polystyrene calibration can be considered as an upper bound on the absolute $\bar{M}_w$ value.

Introduction

Linear polyurethane block copolymers are normally a condensation product of three monomers: an oligomeric diol, typically a dihydroxy-terminated polyether or polyester with a number-average molecular weight of 500–3000; a diisocyanate that is generally aromatic; and a low molecular weight aliphatic diol chain extender.[1] The final polymer structure is represented as being of the $(AB)_n$ type, where A and B represent so-called hard and soft segments. The precise definitions of the hard and soft segments vary in the literature; in this investigation the soft segment is defined as that portion of the polymer chain originating from the polyether or polyester oligomeric diol while the hard segments are either single reacted diisocyanate units or reaction products of the diisocyanate and chain-extender monomers. A typical structure of a polyurethane block copolymer is shown in Figure 1. The terms hard and soft segments arise from the fact that at room or service temperature the soft segments are normally in a rubbery or viscous state while the hard segments are crystalline or glassy. In the solid state the hard and soft segments tend to phase separate to produce hard- and

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