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# Articles

## Synthesis and Characterization of a Model Saturated Hydrocarbon Diblock Copolymer

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ABSTRACT: A series of nearly symmetric anionically polymerized *cis*-1,4-polyisoprene–1,2-polybutadiene (1,4PI–1,2PB) diblock copolymers were hydrogenated by using a heterogeneous palladium catalyst, producing a model poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer. Differential scanning calorimetry, small-angle X-ray scattering, and observation of flow behavior have been used to establish the phase state of these monodisperse materials which contain approximately 54% by weight 1,4PI or PEP and range from $M_w$ = 33 000 to 111 000. All 1,4PI-1,2PB samples were found to be homogeneous. For PEP–PEE, an upper microphase separation transition (MST) temperature occurs at 91 ± 10 °C for a $M_w$ = 53 600 sample. Decreasing or increasing molecular weight lowers or raises the MST temperature as predicted by theory. These findings are not accounted for by classical theories which describe the mixing thermodynamics of nonpolar polymers solely in terms of a difference in cohesive energy densities.

## I. Introduction

A preponderance of past fundamental studies aimed at elucidating the structure and properties of block copolymers have relied upon polystyrene–polydiene substrates. Recent examples include the small-angle X-ray and electron microscopy studies of star block copolymers by Thomas et al.[1,2] and Hashimoto et al.,[3] rheological investigations of di- and triblock copolymers by Morrison et al.[4,5] and Han and Kim,[6] and investigations of homopolymer–block copolymer mixtures by Nojima and Roe.[7] And although polystyrene and polydienes represent an attractive polymer combination for studying a variety of block copolymer related phenomena (e.g., the bicontinuous structure by electron microscopy[2]), use of these materials in the weak segregation limit restricts attention to a rather low molecular weight ($\sim 10^4$) regime. This, in part, precludes evaluation of statistical thermodynamic theories developed for high molecular weight polymers[8,9] and limits rheological studies to the unentangled state. With these limitations in mind, and with a desire to investigate order and disorder in entangled, high molecular weight block copolymers, we have directed some of our efforts at developing more suitable materials with which to pursue these objectives.

The work reported in this paper follows the previous development of another model block copolymer system.[10] Then, the anionic polymerization of 1,4-polybutadiene–1,2-polybutadiene (1,4PB–1,2PB) diblock copolymers led to a series of small-angle neutron scattering (SANS)[11] and rheological[12] studies of block copolymers near the microphase separation transition (MST). The 1,4PB–1,2PB material is characterized by a variety of useful properties, including a low glass transition temperature and a modest molecular weight for microphase separation (e.g., a symmetric $M_w$ = 70 000 diblock copolymer microphase separates at about 100 °C). Also, perdeuteriobutadiene is readily available, easily purified, and anionically polymerizable, allowing for the production of SANS samples. However, along with these desirable features, use of polybutadienes necessitates coping with potentially serious complications deriving from a high concentration of unsaturated repeat units. Exposure to oxygen, light, and heat readily induces cross-linking, rendering such materials useless. Although these complications can be avoided by proper storage and handling, the interpretation of unexpected phenomena, such as the SANS behavior of the asymmetric 1,4PB–1,2PB diblock copolymer[11] or the low-frequency rheological properties of these materials in the disordered state,[12] will never completely escape suspicion. Furthermore, the long-term stability and experimental temperature range afforded by these substances are limited.

In this paper we report the successful development of a new, fully saturated, hydrocarbon diblock copolymer which retains all the desirable properties characterizing 1,4PB–1,2PB. In addition, the elimination of unsaturation endows this polymer with significantly greater stability toward thermal, oxidative, and radiation-induced degradation relative to our previous model system. This material is prepared by hydrogenating anionically polymerized *cis*-1,4-polyisoprene–1,2-polybutadiene thus producing poly(ethylenepropylene)–poly(ethylethylene) diblock copolymer, denoted PEP–PEE.

We demonstrate here that a nearly symmetric PEP–PEE diblock copolymer is characterized by an upper microphase separation transition temperature of 91 ± 10 °C at a molecular weight of $M_w$ = 53 600. Increasing or decreasing the molecular weight is shown to raise and lower the MST temperature, respectively, in qualitative agreement with current theory. This material should be quite useful in examining the thermodynamics and dynamics of ordered and disordered block copolymers.

## II. Experimental Section

**A. Materials.** Butadiene (Matheson, instrument purity) and isoprene (Aldrich, gold label) monomers were purified by successive vacuum distillations from dibutylmagnesium, and subsequently *n*-butyllithium. Cyclohexane (Aldrich, anhydrous 99+%) was either used as received (hydrogenation reactions) or further purified by distillation from excess polystyryllithium (anionic polymerizations). *sec*-Butyllithium in cyclohexane

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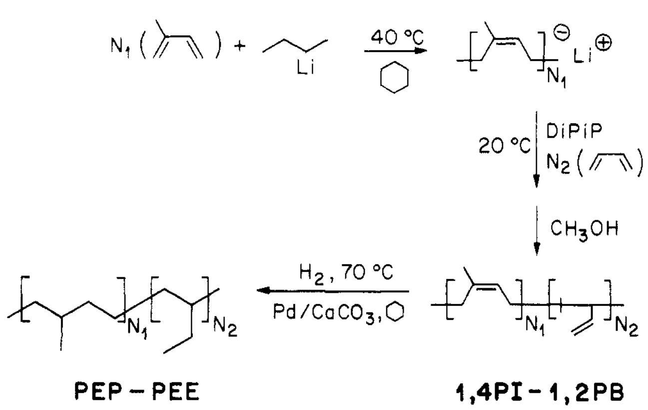

**Figure 1.** Schematic illustration of reaction path for the production of PEP–PEE diblock copolymer.

(Aldrich) was used as received; active initiator concentration (ca. 1.3 M) was determined by the Gilman double-titration method. 1,2-Dipiperidinoethane (DIPIP) (Aldrich 98%) was stirred over calcium hydride, while under vacuum, for several days, followed by vacuum distillation; the purified DIPIP was stored under purified argon. Methanol (J. T. Baker) was used as received (polymer precipitations) or deoxygenated by successively freezing, vacuum pumping, and thawing (polymerization termination).

**B. Synthesis.** Four diblock copolymerizations of isoprene and butadiene were conducted under purified argon in a Pyrex reactor fitted with Viton O-ring sealed joints and Teflon or Viton O-ring sealed valves. Cyclohexane was distilled directly into the reactor and brought to 40 °C. An aliquot of *sec*-butyllithium was added to the well-stirred solvent with a gas-tight syringe (Hamilton), followed by the immediate addition of isoprene. Total anion concentration ranged from $1.1 \times 10^{-3}$ to $2.4 \times 10^{-3}$ M $L^{-1}$. Polymerization of the isoprene was evidenced by a rise in temperature (ca. 2 °C), which peaked after approximately 20 min, and a drop in the reactor pressure. After 3 h (considerably longer than either the anticipated time for >99% conversion or the time at which the reactor pressure ceases dropping) the temperature was reduced to 18 °C and a five-to-one molar ratio of DIPIP relative to the lithium concentration was added to the solution by syringe, followed by addition of the butadiene monomer. Polymerization of butadiene under these conditions yields >99% atactic 1,2-addition.[13] Polymerization of butadiene was also manifested by a slight temperature rise (ca. 1 °C) which peaked after 30–60 min and by a drop in the reactor pressure. Reactions were terminated after 7–18 h, depending on the anion concentration, by addition of several milliliters of degassed methanol. The *cis*-1,4-polyisoprene–1,2-polybutadiene diblock copolymers, denoted 1,4PI–1,2PB, were recovered by precipitation in methanol, vacuum dried, and stored in the absence of light under purified argon at −20 °C. 1,4PI and 1,2PB homopolymers were prepared by similar techniques.

**C. Hydrogenation.** Each of the 1,4PI–1,2PB diblock copolymers and homopolymers was hydrogenated in a 2-L Parr reactor with two parts, by weight, of a calcium carbonate supported palladium catalyst (Strem) for each part unsaturated polymer. Polydiene–cyclohexane solutions (2% w/v) were prepared under purified argon and added to the catalyst contained in the reactor. The heterogeneous mixture was then rigorously stirred, pressurized with hydrogen (500 PSI), and brought to 70 °C for 24 h. Recovery of the saturated polymer product was accomplished by filtration (0.2-μm filter), precipitation in methanol, and vacuum drying. Hydrogenated polymers were stored under purified argon. A more detailed discussion of this heterogeneous catalytic hydrogenation reaction can be found in a recent publication.[14]

A schematic summary of the overall reaction path for the preparation of PEP–PEE is provided in Figure 1.

**D. Molecular Characterization.** Room temperature $^{13}C$ and $^{1}H$ NMR spectra were obtained from 20% (w/v) $CDCl_3$ solutions of the saturated and unsaturated diblock copolymers and homopolymers by using a JEOL FX90Q spectrometer; TMS was added to the solutions for use as an internal reference. Number-average molecular weights were determined for the hydrogenated diblock copolymers with a Wescan 231 membrane osmometer, operated at 30 °C with reagent grade toluene (Aldrich). A minimum of four solutions ranging in concentration from 1 to 8 g $L^{-1}$ were measured for each material. Size exclusion chromatography (SEC) traces were obtained from an instrument fitted with dual Zorbax (Du Pont) size exclusion columns and operated at room temperature with THF as the mobile phase at a flow rate of 1 mL per min. Elution times were monitored with a differential refractometer (Waters) following injection of 100 μL of 0.1% (w/v) polymer solutions. The instrument was calibrated by using a series of monodisperse polystyrene standards (Pressure Chemical Co.).

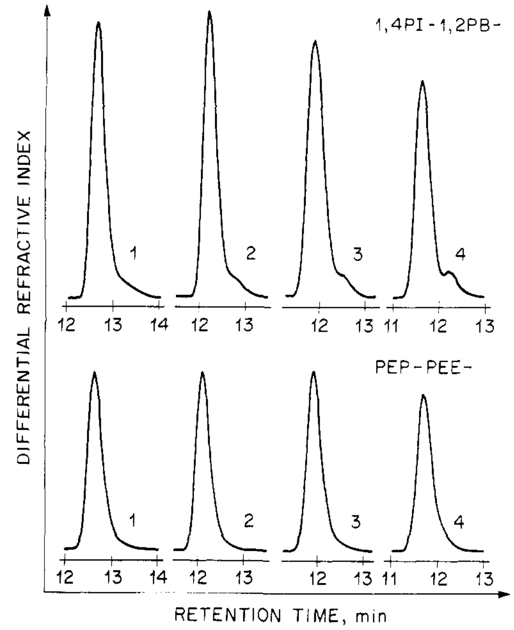

**Figure 2.** Size exclusion chromatographs for the polydiene (1,4PI–1,2PB) and saturated hydrocarbon (PEP–PEE) diblock copolymers.

**E. Physical Characterization.** PEP–PEE and 1,4PI–1,2PB diblock copolymers, and the corresponding homopolymers, were examined by differential scanning calorimetry (DSC) between −100 and 25 °C by using a Perkin-Elmer System DSC-7. Specimens (ca. 15 mg) were rapidly cooled (ca. 100 °C/min) below −100 °C and subsequently evaluated at a heating rate of 15 °C/min.

The qualitative flow behavior of the diblock copolymers was assessed by placing approximately 0.3-g specimens of each of the four saturated and unsaturated materials on a glass slide and photographically documenting the shape (i.e. form) of the specimens as a function of time and temperature.

Small-angle X-ray scattering (SAXS) measurements were conducted on Beamline I-4 at the Stanford Synchrotron Radiation Laboratory. The characteristics of the SAXS instrument have been described elsewhere.[15] SAXS specimens of the saturated block copolymers were prepared by placing the copolymer in a 1-mm-thick cell comprised of a brass spacer fitted with Kapton windows. Loaded cells were placed into a Mettler FP85 hot stage, which contains 2-mm holes through the upper and lower heaters through which the X-ray beam passed. Helium was circulated through the hot stage to minimize polymer degradation. The sample temperature was controlled to within 0.2 °C.

Homopolymer densities were determined by using the density gradient column technique following our previously described procedures:[16] $\rho_{1,4PI} = 0.900$; $\rho_{1,2PB} = 0.887$; $\rho_{PEP} = 0.854$; $\rho_{PEE} = 0.869$ g $cm^{-3}$.

## III. Results and Analysis

**A. Molecular Characterization.** SEC results for the four 1,4PI–1,2PB diblock copolymers are presented in Figure 2. Each of these chromatographs is characterized by a monodisperse main peak and a small shoulder, or peak, at longer retention times. The low molecular weight (long retention time) component derives from homopolyisoprene generated by the spurious termination of a small percentage (≲5%) of the polyisoprenyllithium prior to the addition of butadiene. As evident in Figure 2, the fraction

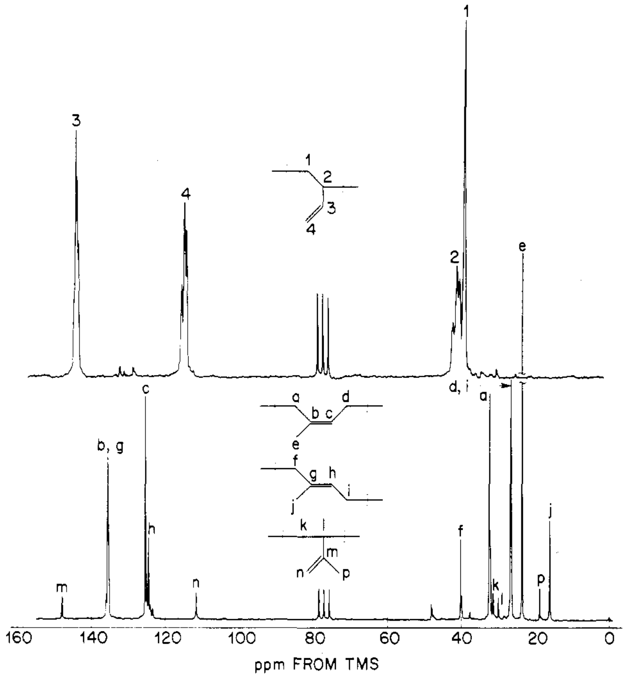

**Figure 3.** $^{13}C$ NMR solution ($CDCl_3$) spectra for 1,2PB (upper trace) and 1,4PI (lower trace). The latter is a random copolymer of cis (75%) and trans (20%) 1,4 and 3,4 (5%) isomers.

**Table I**
**1,4PI–1,2PB Characterization Results**[a,b]

| | | microstructure, % | | | |
|---|---|---|---|---|---|
| | | 1,4PI | | | 1,2PB |
| sample | wt %, 1,4PI | cis-1,4 | trans-1,4 | 3,4 | 1,2 |
| 1,4PI–1,2PB-1 | 56 | 75 | 20 | 5 | >98 |
| 1,4PI–1,2PB-2 | 54 | 75 | 20 | 5 | >98 |
| 1,4PI–1,2PB-3 | 56 | 75 | 19 | 5 | >98 |
| 1,4PI–1,2PB-4 | 57 | 77 | 19 | 4 | >98 |
| 1,4PI[c] | 100 | 71 | 22 | 7 | |
| 1,2PB | 0 | | | | >98 |

[a] Based on $^{13}C$ NMR. [b] Molecular weights and polydispersities are as listed in Table II. [c] Synthesized in benzene.

of homopolymer systematically increases with increasing molecular weight. This result coincides with a decrease in anion concentration, strongly suggesting anion deactivation by reaction with impurities on the reactor surface, in the solvent, or in the butadiene monomer. We believe the former to be the most likely source of this minor complication.

Overall polydiene compositions were determined by $^{13}C$ NMR. As indicated in Figures 3 and 4 the 1,4PI–1,2PB $^{13}C$ NMR spectra constitute a combination of the corresponding homopolymer spectra, thus providing a direct method for determining the polydiene block copolymer compositions. These results are listed in Table I, along with microstructural information determined for the polyisoprene and polybutadiene blocks by conventional methods.[17] Together, the SEC and $^{13}C$ NMR results demonstrate that the block copolymerization reaction outlined in Figure 1 proceeds smoothly and quantitatively.

The degree of polydiene block copolymer hydrogenation was confirmed by $^{13}C$ and $^{1}H$ NMR to be >99.5%, as demonstrated in Figure 4. This result is comparable to that obtained for the hydrogenation of 1,2-polybutadiene as reported elsewhere.[14] Thus, the incorporation of different polydienes within a given polymer chain does not influence the efficiency of these heterogeneous catalytic hydrogenation reactions. However, we have found an unexpected and beneficial effect when hydrogenating 1,4PI–1,2PB polymers. Comparison of the SEC results for the saturated diblock copolymers with the unsaturated precursor materials shown in Figure 2 reveals that hydrogenation effectively removes the small amount of homopolyisoprene present in the starting material.[18] This is also manifested as a slight shift in the average $^{13}C$ NMR determined composition for the PEP–PEE diblock copolymers (Table II) versus that determined for the polydiene precursors. Presumably the PEP polymer has a higher affinity for the catalyst surface than the PEP–PEE copolymer, thereby effecting a separation through selective adsorption following hydrogenation. Regardless of the mechanism, the resulting product is essentially pure diblock copolymer (Figure 2).

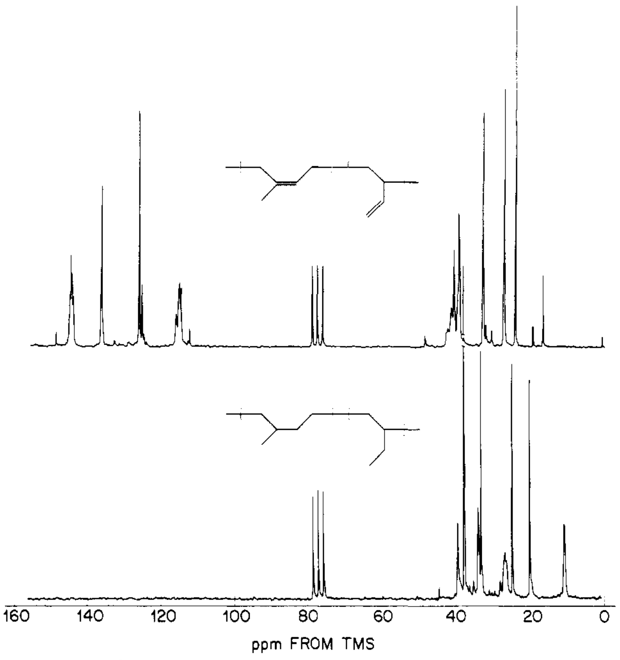

**Figure 4.** $^{13}C$ NMR solution ($CDCl_3$) spectra for diblock copolymer 1,4PI–1,2PB-4 (upper trace) and the corresponding hydrogenated sample PEP–PEE-4. The upper spectrum can be represented by a linear combination of the homopolymer spectra illustrated in Figure 3, from which the 1,4PI–1,2PB compositions have been determined. A saturation efficiency of >99% is evidenced by the absence of resonances above 100 ppm in the lower spectrum.

**Table II**
**PEP–PEE Characterization Results**

| sample | $10^3 M_n$[a] | $M_w/M_n$[b] | wt % PEP[c] |
|---|---|---|---|
| PEP–PEE-1 | $31._5$ | 1.05 | 53 |
| PEP–PEE-2 | $50._1$ | 1.07 | 56 |
| PEP–PEE-3 | $81._2$ | 1.05 | 53 |
| PEP–PEE-4 | 106 | 1.07 | 54 |
| PEP | $86._1$ | 1.07 | 100 |
| PEE[d] | 172 | 1.03 | 0 |

[a] Membrane osmometry. [b] Size exclusion chromatography. [c] $^{13}C$ NMR. [d] Intrinsic viscosity.

PEP–PEE diblock copolymer number-average molecular weights were determined by membrane osmometry; these results are listed in Table II. To a close approximation the corresponding 1,4PI–1,2PB materials listed in Table I are characterized by the same number-average molecular weights, $M_n$, since the hydrogenation reaction does not influence the carbon–carbon bond structure. Polydispersity indices were obtained for the saturated polymers from a SEC calibration curve constructed from the peak retention times shown in Figure 2 and the $M_n$ values listed in Table II. The resulting linear calibration curve yielded the polydispersity indices listed in Table II; within ex-

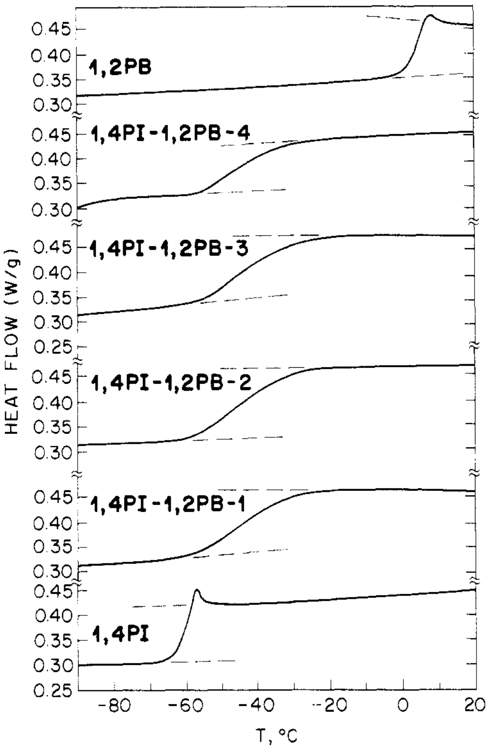

**Figure 5.** Differential scanning calorimetry traces for the polydiene diblock copolymers and the corresponding homopolymers. All six specimens are characterized by a single glass transition, indicative of homogeneity. Dashed lines are extensions of glassy and rubbery $C_p$ behavior above and below $T_g$.

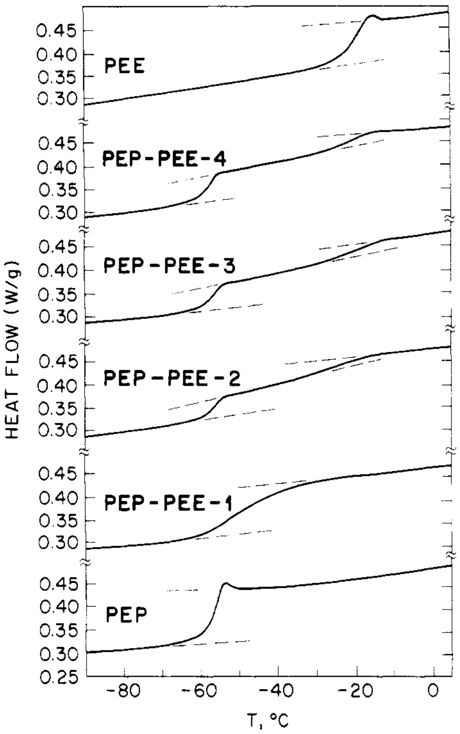

**Figure 6.** Differential scanning calorimetry traces for the saturated hydrocarbon diblock copolymers and the corresponding homopolymers. Homogeneous sample PEP-PEE-1 exhibits a single broad glass transition while the other three microphase-separated diblocks are characterized by two sharper transitions. Dashed lines are as defined in Figure 5.

perimental error the same results were achieved from a polystyrene-based calibration curve.

Saturated block copolymer compositions were determined by $^{13}C$ NMR, using chemical shift assignments established from PEP and PEE homopolymer solution spectra. These results are also listed in Table II. For all practical purposes the entire set of PEP–PEE diblock copolymers is characterized by a single composition, $f_{PEP} = 0.54 \pm 0.02$.

**B. Physical Characterization.** We have made use of three characterization methods in establishing whether the 1,4PI–1,2PB and PEP–PEE block copolymers are ordered (microphase separated) or disordered (homogeneous): differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and a simple visual determination of flow behavior.

In Figures 5 and 6 we present DSC results for the 1,4PI–1,2PB and PEP–PEE diblock copolymers, respectively, along with data for the four corresponding homopolymers. The four polydiene diblock copolymers are essentially thermally indistinguishable, each exhibiting a single broad glass transition, $T_g \cong -40$ °C, where $T_g$ is defined as the temperature midway between the jump in heat capacity $\Delta C_p$ associated with the glass transition. This behavior resembles that previously observed for homogeneous 1,2-polybutadiene–1,4-polybutadiene diblock copolymers.[10] However, contrary to the previous study, where increasing molecular weight initially broadened the glass transition and subsequently split the DSC response into two distinct transitions due to microphase separation, a three and one-half times increase in the 1,4PI–1,2PB molecular weight produces no perceptible change in thermal behavior. These results indicate that all four of these polymers are thermodynamically homogeneous.

Hydrogenation of the unsaturated diblock copolymers produces various modifications in physical properties. A comparison of Figures 5 and 6 reveals a change in the glass transition of 1,2-polybutadiene and *cis*-1,4-polyisoprene with hydrogenation, i.e., $T_{g,1,2PB} \cong 0$ versus $T_{g,PEE} \cong -20$ °C and $T_{g,1,4PI} \cong -60$ versus $T_{g,PEP} \cong -56$ °C. Along with these modifications the PEP–PEE materials are thermodynamically more complex than the polydiene block copolymers. Sample PEP–PEE-1 exhibits a single broad glass transition (Figure 6) analogous to the DSC traces obtained for each of the 1,4PI–1,2PB samples (Figure 5). However, increasing molecular weight, i.e., samples PEP–PEE-2, -3, and -4, leads to the development of two discernible glass transitions near the glass transition temperatures for PEP and PEE. This behavior follows that previously documented for polybutadiene diblock copolymers[10] and is indicative of an ordered (microphase separated) state.

Because PEP and PEE are chemical isomers characterized by similar densities (see Experimental Section) PEP–PEE block copolymers are difficult to study by SAXS using conventional X-ray sources. However, the signal-to-noise afforded by the intense beam of X-rays produced at synchrotron sources is sufficient for the evaluation of the phase state in these materials. In Figure 7 we present SAXS traces obtained at room temperature (28 °C) from each of the PEP–PEE diblock copolymers. The strong upturn in intensity as $q \rightarrow 0$ derives from impurity scattering (e.g., residual hydrogenation catalyst); this effect is greatly magnified relative to the peak intensity due to the miniscule block copolymer scattering contrast factor. Samples PEP–PEE-4, -3, and -2 exhibit distinct scattering maxima, characteristic of an ordered block copolymer. Decreasing molecular weight leads to an increase in the peak scattering wavevector $q^*$ ($q = 4\pi\lambda^{-1} \sin \theta/2$, where $\lambda$ and $\theta$ are the radiation wavelength and scattering angle, respectively) as predicted by theory.[8,19] This trend continues upon further lowering the molecular weight, i.e., for sample PEP–PEE-1, but with an associated dramatic drop in the peak intensity, in qualitative agreement with

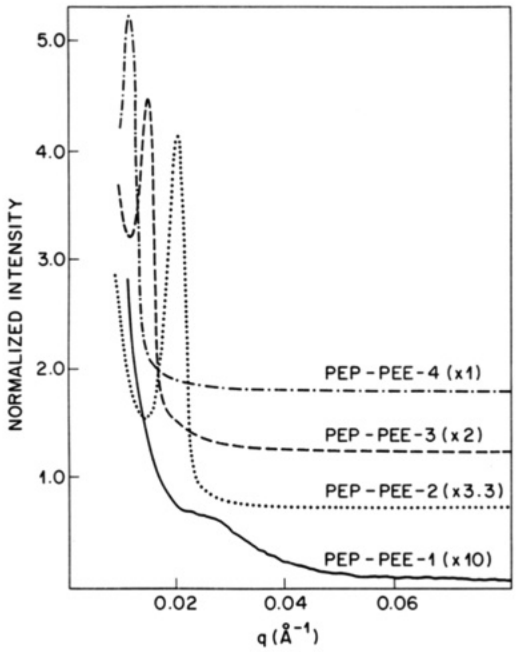

**Figure 7.** Small-angle X-ray scattering traces obtained at 28 °C for the saturated hydrocarbon diblock copolymers. Relative intensities have been scaled as indicated in the parentheses in order to facilitate comparison. The large difference in peak intensity between samples PEP–PEE-2, -3, and -4 and PEP–PEE-1 is a manifestation of microphase separation and homogeneity.

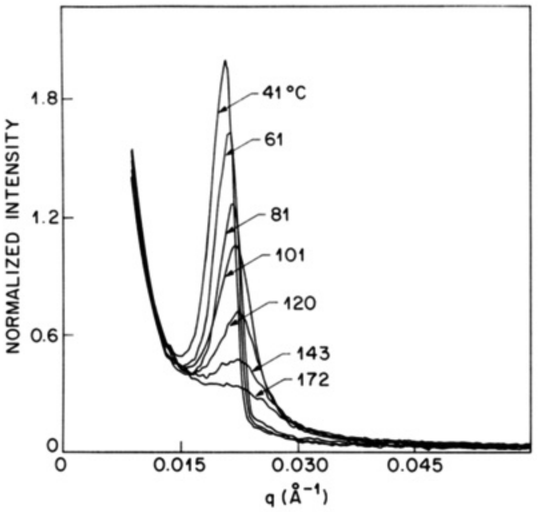

**Figure 8.** Temperature dependence of the small-angle scattering of X-rays from sample PEP–PEE-2. An upper microphase separation transition temperature lies between 81 and 101 °C as evidenced by the discontinuity in line shape above and below these temperatures.

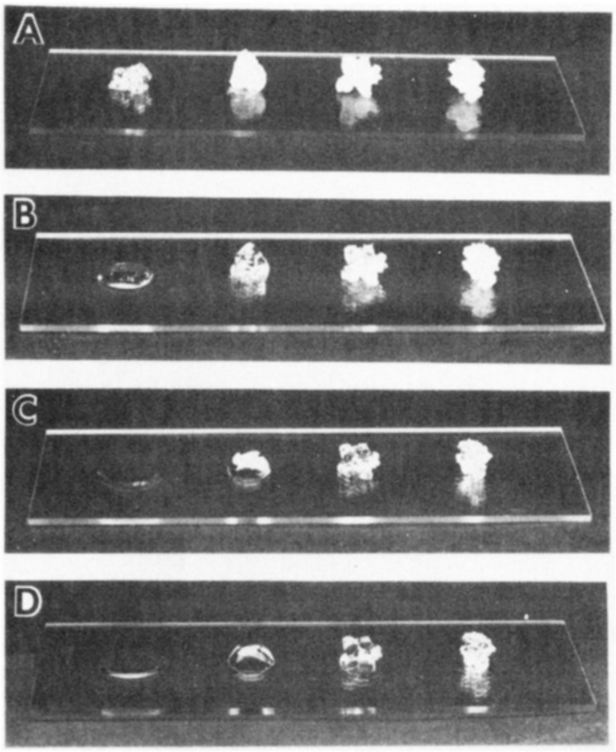

**Figure 9.** Room temperature flow behavior of the PEP–PEE diblock copolymers (increasing molecular weight from left to right) at 22 °C: (A) immediately following preparation; after (B) 1 day, (C) 15 days, (D) 32 days. Only homogeneous sample PEP–PEE-1 attains a liquidlike profile.

Leibler's[8] prediction for disordered diblock copolymer. These isothermal SAXS results are consistent with the DSC data; i.e., at room temperature sample PEP–PEE-1 is disordered and the three higher molecular weight PEP–PEE specimens are ordered.

We have determined that the order–disorder (microphase separation) transition (MST) for the PEP–PEE diblock copolymer corresponds to an upper microphase separation temperature (analogous to UCST behavior for homopolymer mixtures) by recording the SAXS pattern for PEP–PEE-2 as a function of temperature. These results (Figure 8) can be divided into two categories: low temperature (41, 61, and 81 °C) and high temperature (101, 120, 143, and 172 °C). At the highest measurement temperature (172 °C) the SAXS pattern for PEP–PEE-2 closely resembles that obtained at room temperature from sample PEP–PEE-1. Lowering the temperature in the high-temperature regime produces an increase in the peak intensity, without significantly influencing the peak shape. Between 101 and 81 °C the peak noticeably sharpens, in addition to increasing in intensity. Further cooling in the low-temperature regime produces additional intensity and narrowing, but without changing the qualitative peak shape. This transition from high- to low-temperature regimes is particularly apparent on the high-$q$ side of these reflections. From these results we can deduce that sample PEP–PEE-2 is characterized by an upper MST temperature between 81 and 101 °C and, therefore, that the Flory–Huggins parameter $\chi$ varies linearly with inverse temperature.

On the basis of our previous experience with polybutadiene diblock copolymers,[10] we expect a dramatic difference in the long-time relaxation behavior of disordered versus ordered PEP–PEE diblock copolymers. Figures 9 and 10 document these differences. Comparison of the room temperature flow behavior (Figure 9) reveals a qualitative difference in the rheological behavior of sample PEP–PEE-1 relative to the three high molecular weight materials. This is consistent with our previous conclusions; i.e., sample PEP–PEE-1 is disordered whereas PEP–PEE-2, -3, and -4 are ordered at room temperature. Here we note that all four 1,4PI–1,2PB diblock copolymers exhibit analogous flow behaviors to that displayed by PEP–PEE-1 (Figure 9), further corroborating the DSC results presented in Figure 5. In Figure 10 we illustrate the effects of temperature on the flow behavior of the PEP–PEE samples. Consistent with the SAXS results (Figure 8), this property changes qualitatively for sample PEP–PEE-2 between 75 and 125 °C, due to the existence of the microphase separation transition.[20] However, increasing the temperature to as high as 220 °C fails to disorder sample PEP–PEE-3 (see Figure 10). This simple

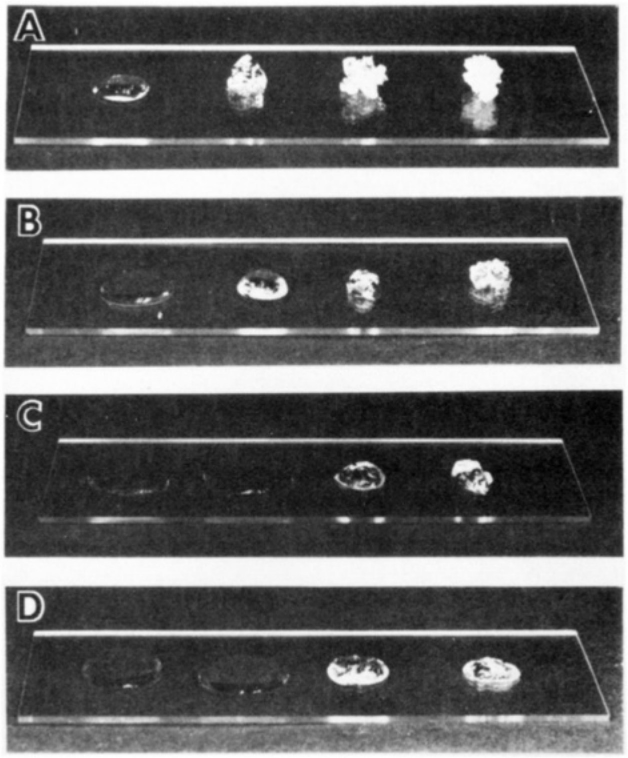

**Figure 10.** Temperature dependence of the 1-day flow behavior of the PEP–PEE diblock copolymers (increasing molecular weight from left to right): (A) 22 °C (see Figure 9); (B) 75 °C; (C) 125 °C; (D) 220 °C. The qualitative flow characteristics of sample PEP–PEE-2 change between 75 and 125 °C, consistent with the existence of an upper microphase separation transition temperature.

method of estimating the molecular weight and temperature for microphase separation (Figures 9 and 10) is invaluable when developing a new model block copolymer system. Other more time consuming techniques, such as small-angle scattering and rheometry, are best utilized for investigating the quantitative aspects of the MST, after the qualitative properties have been established.

## IV. Discussion

The results presented in the previous sections can be summarized as follows. Nearly symmetric ($f = 0.54$) diblock copolymers of *cis*-1,4-polyisoprene and 1,2-polybutadiene (1,4PI–1,2PB) up to $M_w = 111\,000$ are homogeneous. Poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymer, obtained by hydrogenating 1,4PI–1,2PB, exhibits an upper microphase separation transition temperature at 91 ± 10 °C for $M_w = 53\,600$. In this section we briefly discuss these results in the context of the mean-field theory for polymer–polymer mixing.

Our findings regarding the miscibility of *cis*-1,4-polyisoprene (1,4PI) and atactic 1,2-polybutadiene (1,2PB) diblock copolymers are not surprising. Miscibility of natural rubber and "sodium butadiene rubber" was reported over 25 years ago by Bartenev and Kongarov[21] on the basis of dilatometric measurements. The reported glass transition temperature of the polybutadiene component (−48 °C) indicates a composition of approximately 50% 1,2-vinyl units; this is consistent with the microstructure obtained from the sodium-catalyzed polymerization of butadiene.[22]

Cohen and co-workers[23,24] have also documented miscibility in binary mixtures of 1,4PI with "high-vinyl" (64% 1,2-addition)[23] and 1,2 (99%)[24] polybutadiene which was discussed by using a solubility parameter analysis. More recently, Roland[25] examined another series of 1,4PI–high vinyl (86% 1,2-addition) polybutadiene mixtures by dynamic mechanical (tensile) testing and DSC and concluded that these materials mixed over all compositions. Thus, we expected all our 1,4PI–1,2PB diblock copolymers (>99% 1,2-addition in the polybutadiene block) to be homogeneous since the molecular weight of 1,4PI–1,2PB-4, our highest molecular weight diblock copolymer, is less than the previously studied binary mixture molecular weights. In fact, we also have obtained homogeneous mixtures from 1,4PI and 1,2PB homopolymers ($M_w \cong 200\,000$) for compositions ranging from 10 to 90% by volume polyisoprene.

**Table III**
**Hydrocarbon Polymer Segment–Segment Interaction Parameters**[a]

| system | $10^3\chi_{\text{exptl}}$ | $10^3\chi_{\text{calcd}}$ eq 1 | $10^3\chi_{\text{calcd}}$ eq 2[d] | $T$, K | ref |
|---|---|---|---|---|---|
| dPEE–PEE | $0.9_1$[b] | 0.60 | | 296 | 16 |
| d1,2PB–1,2PB | $0.7_1$[b] | 0.54 | | 296 | 16 |
| d1,4PB–1,4PB | $0.5_9$[b] | 0.42 | | 335 | 31 |
| 1,4PI–1,2PB | <0.4[b] | 3.2 | 28 (27) | 293 | 25 |
| 1,4PI–1,4PB | ~2[c] | 0.44 | 0.014 (0.55) | 293 | 32 |
| 1,2PB–1,4PB | 10[c] | 1.0 | 25 (36) | 298 | 12 |
| PEP–PEE | 12[c] | 2.5 | 0.34 (0.19) | 373 | |
| PS–3,4PI | 170[c] | 140 | 190 (160) | 398 | 33 |

[a] Based on approximately 50/50 (v/v) composition mixtures or diblock copolymers. [b] Binary homopolymer mixture. [c] Diblock copolymer. [d] Based on Small's (and Hoy's) group contribution values.

We are unaware of any reports dealing with PEP and PEE miscibility prior to this work. In the remainder of this section we evaluate the thermodynamics of 1,4PI–1,2PB and PEP–PEE in the context of the reported phase behavior for other mixtures of nonpolar hydrocarbon polymers.

In Table III are listed eight pairs of hydrocarbon polymers for which experimental and calculated estimates of the segment–segment interaction parameter $\chi$ can be made. The experimental parameters $\chi_{\text{exptl}}$ each correspond to an approximately 50/50 (v/v) composition of binary mixture or diblock copolymer as determined by SANS, SAXS, light scattering, DSC, or dynamic mechanical analysis. We have assumed that the critical point for phase separation and microphase separation is given by $(\chi N)_c = 2$ and $(\chi N)_c = 10.5$, for homopolymer mixtures[26] and diblock copolymers,[8] respectively. This mean-field treatment neglects fluctuation effects, which are particularly important when dealing with block copolymers.[9] Nevertheless, within the context of the crude analysis discussed below, such effects are insignificant. The estimated $\chi_{\text{exptl}}$ values have been collected into three groups: isotopes, isomers and chemically similar pairs, and chemically distinct pairs. We initially discuss the first and third groups.

The heat generated by mixing nonpolar (e.g., hydrocarbon) polymers derives from purely dispersion interactions. For the simplest case listed in Table III, isotopic mixtures, we have recently shown that the segment–segment interaction parameter can be estimated by[16]

$$\chi = \frac{2\pi^2 I}{3k_B T}\left[\left(\frac{\alpha}{v}\right)_1 - \left(\frac{\alpha}{v}\right)_2\right]^2 \tag{1}$$

where $(\alpha/v)$ and $I$ represent the segment polarizability-to-volume ratio and ionization potential, respectively, and $k_B$ is the Boltzmann constant. Comparison of $\chi_{\text{exptl}}$ and $\chi_{\text{calcd}}$ as determined by eq 1 (Table III) shows that the interaction parameter for deuterated and protonated polymers is reasonably predictable.

For chemically different components, $\chi$ can also be calculated by using solubility parameters $\delta_i$[27]

$$\chi = \frac{v}{k_B T}(\delta_1 - \delta_2)^2 \qquad (2)$$

where, for example, $\delta = \sum_i F_i/v$ is estimable from tabulated group contributions $F_i$. Because calculation of $\alpha/v$ and $\delta$ requires an accurate knowledge of $v$, i.e., density, only those polymer for which we have such information are included in Table III. Computed values of $\chi_{\text{calcd}}$ based on eq 2, from the values for $F_i$ provided by Small and Hoy (given in parenthesis), are listed in Table III, along with the predictions of eq 1.

Polystyrene and polydienes are among the least miscible hydrocarbon polymer pairs, as demonstrated by the relative magnitude of $\chi_{\text{exptl}}$ listed for polystyrene (PS) and 3,4-polyisoprene (3,4PI) in Table III. Correspondingly, PS and polydienes are characterized by rather different cohesive energy densities, i.e., $I\alpha^2/v$ or $\delta^2$. Both eq 1 and 2 predict the relative magnitude of the segment–segment interaction parameter found experimentally for PS and 3,4PI.

In contrast with the isotopes and PS–3,4PI (a chemically distinct pair), the thermodynamics of the isomers and chemically similar polymer pairs are not generally anticipated by either eq 1 or 2. Although these relationships are not expected to be perfectly quantitative, agreement within roughly a factor of 2 can be expected, if the mixture under consideration conforms to the assumptions implicit in their derivation. These include purely nonspecific interactions, a negligible excess entropy of mixing, and a geometric mean interaction between species 1 and 2. We believe these assumptions may be violated by the mixtures of isomers and chemically related hydrocarbon polymers. In our opinion, the similarity in pure component cohesive energy densities in this class of mixtures magnifies the relative contribution of the excess thermodynamic quantities to $\chi$. For example, small variations in local polymer conformation induced by optimization of segment packing (possibly giving $\Delta V^{\text{ex}} \neq 0$) could significantly alter the apparent interaction parameter relative to that anticipated by eq 1 and 2. Comparison of the experimental and predicted $\chi$ values in Table III suggests that such effects can either increase or decrease miscibility. Most dramatic is the phase behavior of *cis*-1,4-polyisoprene and 1,2-polybutadiene. It is possible that this system is actually characterized by a *negative* interaction parameter despite the fact that the constituents are pure hydrocarbons; this implies that the net packing entropy and energy of the mixture are more favorable than those of the pure components, which is certainly feasible. Whereas eq 1 and 2 significantly overestimate $\chi$ for 1,4PI and 1,2PB, they greatly underestimate this parameter for PEP and PEE.

Why then are such effects not encountered with the isotopic mixtures, which are governed by the smallest known differences in cohesive energy densities? Isotopes represent structurally symmetric chemical analogues, characterized by essentially identical shapes and packing behaviors, e.g., deuterated and normal polymer exhibit the same glass transition temperature.[10] For this reason isotopic mixtures are ideal systems with which to study the statistical thermodynamics of polymer–polymer mixing without the complications presently being discussed, as detailed elsewhere.[28] At the other extreme are mixtures with a large cohesive energy density difference. Here, subtle variations in segment packing do not alter the qualitative nature of the interactions, and the validity of eq 1 and 2 is recovered.

Although we cannot presently provide a detailed explanation for the curious phase behavior exhibited by *cis*-1,4-polyisoprene and 1,2-polybutadiene, the comparisons in Table III suggest reasons other than a simple similarity of cohesive energy densities.[25] This in turn could present new strategies for designing miscible mixtures of chemically related compounds. We have recently learned that Lohse et al.[29] are also pursuing this objective using various combinations of saturated hydrocarbon polymers.

## V. Summary

Our objective in this work was to develop a model diblock copolymer system with the characteristics outlined in the Introduction. This goal is fulfilled by the PEP–PEE diblock copolymer as evidenced by the results discussed in the previous sections. Because this material is a completely saturated hydrocarbon, we expect a minimal degree of oxidative or radiation-induced degradation or cross-linking to occur under moderate experimental conditions, e.g., during rheological or neutron scattering experimentation for $T < 200$ °C. The molecular weight at which a symmetric diblock copolymer of PEP and PEE passes through the microphase separation transition at 91 ± 10 °C (an upper MST temperature) has been shown to be $M_w = 53600$. At this overall molecular weight, both block molecular weights lie significantly above the entanglement molecular weight,[30] placing this material rheologically in the high polymer regime. Additionally, the low block glass transition temperatures ($T_{g,\text{PEE}} \cong -20$ °C and $T_{g,\text{PEP}} \cong -56$ °C) provide a wide temperature range over which the thermodynamics and dynamics of ordered and disordered block copolymer can be investigated.

In conclusion, we have demonstrated that a fully saturated diblock copolymer, poly(ethylenepropylene)–poly(ethylethylene), denoted PEP–PEE, can be readily prepared by the heterogeneous catalytic hydrogenation of anionically polymerized *cis*-1,4-polyisoprene–1,2-polybutadiene diblock copolymer. Also, we have shown that this polymer represents an attractive material with which to investigate the thermodynamics and dynamics of order and disorder in block copolymers.

**Registry No.** (Isoprene)(butadiene) (block copolymer), 109264-12-2.

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# Far-Infrared Study of Hydrogen Bonding in a Semicrystalline Polyurethane

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ABSTRACT: We have used far-infrared spectroscopy to probe the hydrogen bond vibrational mode of a semicrystalline polyurethane. We assign this vibration to a broad band appearing at 101 cm$^{-1}$ in amorphous samples and 107 cm$^{-1}$ in highly ordered samples. Using a rigid-body approximation, we calculate force constants associated with the hydrogen bond stretching to be 0.52 and 0.58 mdyn/Å for the two forms, respectively. In oriented samples, the band shows the appropriate perpendicular dichroism. The band shows sensitivity to both molecular order and temperature. We also assign a band located at 320 cm$^{-1}$ to a O–C–NH–C bending mode coupled to the methylene chain bending. This band also shows sensitivity to chain conformation and packing as well as having high parallel dichroism in oriented samples.

## Introduction

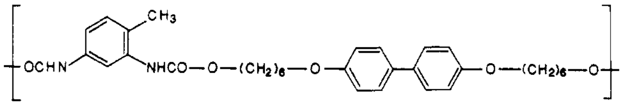
Hydrogen bonding is usually considered the strongest secondary force in the solid state of polymers. The specificity and magnitude of this type of interaction may strongly influence both chain conformation and packing. Because of the importance of hydrogen bonding, its character and its effect on molecular structure and properties have been the topic of numerous studies.[1,2] The hydrogen bond is an essential component of the structure of natural proteins and synthetic polyamides as well as small-molecule association phenomena, intramolecular ring closure, and catalysis.

Due to the incompatibility between the hard and soft segments, polyurethane copolymers undergo microphase separation resulting in hard-segment-rich domains, a soft-segment-rich matrix, and an interphase between them.[3] It is generally accepted that the strength and the elastic behavior of polyurethanes are directly related to the stability of the hydrogen-bonded hard-segment-rich domains, acting as junction points in the network. Extensive research on interurethane hydrogen bonds, based on mid-IR absorption, has been carried out.[4-18] In these studies, the hydrogen bonding characteristics have mainly been interpreted from the observed frequency shifts, either of the NH group or of the C=O group. However, the vibrations between the NH and C=O group which are located in the far-infrared region have attracted comparatively little attention. Direct analysis of the low-frequency vibrations of the hydrogen bonds in synthetic polymers is rare. The most extensive studies have been given to a series of polyamides.[19] To date, we know of no such equivalent studies in polyurethanes.

In this study we present far-infrared spectra of a semicrystalline polyurethane. Among the rich features observed, our results indicate that the band around 105 cm$^{-1}$ can be assigned to a hydrogen bond stretching vibration between the NH and the C=O groups. Its spectroscopic characteristics are sensitive both to the perfection of molecular packing and to temperature changes. In oriented samples it exhibits strong perpendicular dichroism, consistent with its assignment. The band observed at 320 cm$^{-1}$ is assigned to the O–CO–NH–C bending mode coupled with methylene chain bending. It also shows a strong spectroscopic dependence on sample packing and shows high parallel dichroism in oriented samples.

## Experimental Section

The chemical repeat unit of the polyurethane is as follows:



The synthesis and physical characterization of this polymer has been reported elsewhere.[20] The 2,4-toluenediisocyanate (24TDI) used in preparing the polymer was distilled from purified 24TDI (Fluka) to preclude artifacts due to the presence of 2,6-toluenediisocyanate commonly found in commercial 24TDI. The sample polymer used in this study had an intrinsic viscosity of 0.6 and a $M_n$ of 100K, with a polydispersity of 1.6 relative to polystyrene standards as determined by gel permeation chromatography with dimethylacetamide as the eluting solvent. The samples used in our spectroscopic experiments were prepared by pressing the polyurethane at 170 °C between polytetrafluoroethylene sheets. Films prepared at such temperatures were approximately 300 μm in thickness. The infrared data were obtained with a Bruker Model IFS 113v Fourier transform infrared spectrometer. Spectral resolution was maintained at 4 cm$^{-1}$. A deuterated triglycine sulfate (DTGS) detector with a polyethylene

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