Based on the present results and discussion, it is tempting to assume that dissociative electron capture may be an important process in the radiolysis of bulk PVC. This possibility is presently under intensive study in these laboratories, and the results will be reported in the near future together with more detailed discussion of the mechanisms of radiolysis of bulk PVC.

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Spin-Label Investigation of Polyurethane Networks

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ABSTRACT: Two types of polyurethane networks were examined using the spin-label technique. Nitroxide free radicals which are stable under moderate conditions were covalently attached to the network chains of amorphous polymers based on (1) poly(tetramethylene glycol), *p,p′*-diphenylmethane diisocyanate (MDI), trimethylolpropane, and (2) ethylene glycol, MDI, glycerine. Polymer (1) had very low "hard block" content, polymer (2) a very high content. Mechanical properties and differential thermal analysis measurements were made on polymer (1). Electron spin resonance spectra of the samples were obtained in the unstrained, strained, and swollen states. Large differences in the spectra were observed depending on chemical composition, temperature, and state of swelling. Transitions from "frozen" to "rapid motion" type of spectra occurred at 70° for polymer (1), at −10° for polymer (1) swollen to equilibrium, and were unobserved up to 150° for polymer (2). Since the nitroxide label was necessarily adjacent to MDI units, was present in very small concentrations, and experienced no alterations in environment as "soft segments" did, then it is suggested that the spin-label technique is a valuable tool for analyzing microstructure of pseudoamorphous systems.

This paper reports a multiple purpose study involving the paramagnetic labeling of an elastomeric polymer network. In the first phase the feasibility of chemically attaching a stable free radical to a cross-linked polymeric solid was examined. Then, the electron spin resonance (esr) spectra of such a labeled network under various thermodynamic and mechanical conditions were investigated. Finally, consideration was given to the kinds of structural information which might be obtained by a comparison of the spectral characteristics with the chemical composition, mechanical behavior, and thermal properties of the network.

Two types of polyurethane networks were used as the spin-label substrates. These were chosen to facilitate the spin-labeling chemistry and because of the inherent interest in the somewhat anomalous properties of "amorphous" polyurethanes. Both swollen and strained networks of one of the polyurethanes were investigated in addition to the dry material.

Although this study is not exhaustive at this time, some of the initial results are being reported here; indications are that, with cautions, networks may be investigated in a sensitive manner using spin labels.

Background Material and Preliminary Discussion

Spin Labels. With the development of a large series of nitroxide molecules of various shapes and reactivity has come steadily increasing interest in their *in situ* esr spectra as indicators of microscopic environments. Figure 1 shows a nitroxide derivative used in this study, with the free electron indicated. The stability of the nitroxide free radical even in moderately reactive conditions and the synthetic versatility it affords have made it a favorite structural probe for biological systems[1,2] heterogeneous aggregates[3] and, recently, for synthetic macromolecules.[4,5] Three-dimensional synthetic polymer networks have, however, not been studied using spin labels.

Some of the theory for interpreting esr spectra of nitroxide groups in viscous media has been developed.[5-12] Briefly, the esr spectrum of nitroxides in solution is a sharp triplet resulting from the hyperfine coupling of the unpaired electron with the three nuclear spin states of the nitrogen. The "isotropic" value of the hyperfine splitting constant is about 16 G for nitroxides of the Figure 1 type, and obtains when tumbling of the nitroxide group relative to the applied magnetic field is rapid. Figure 2 shows the esr derivative spectrum of 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl, an intermediate used in this work, in dilute chloroform solution and illustrates the characteristic sharp triplet of Lorentzian shapes.

Actually, both the *g* factor and hyperfine interaction tensors of nitroxides are anisotropic, and when the radical's motion with respect to the applied magnetic field is hindered then line broadening and shifts will occur. Spectral analysis becomes rather complex as extreme limiting of the radical's motion takes place. Rotational correlation times, τ_c, of less than 5×10^{-9} sec are required for use of the approximate equations previously devel-

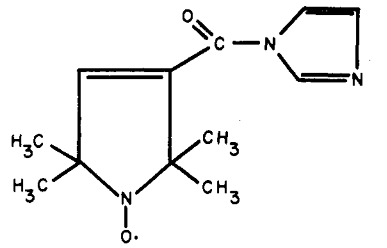

Figure 1. The imidazole derivative of spin label 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl.

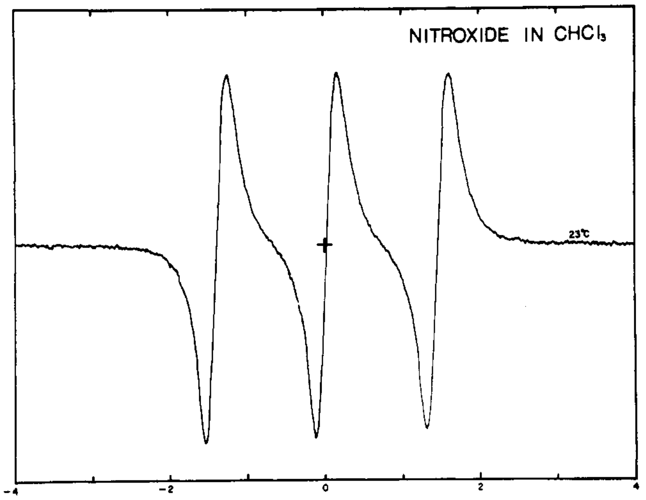

Figure 2. Esr spectrum of 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl in chloroform solution, in tens of gauss from H_0 = 3394.6 G, ν_0 = 9.533 GHz.

oped.[13-15] To illustrate, in Figure 3 is the 23° esr spectrum of a 20% chloroform solution of a spin-labeled poly(tetramethylene oxide) which was used in the present study. One nitroxide molecule was bonded to each end of this 2030 number-average molecular weight polyether. Figures 2 and 3 are quite similar indicating rapid tumbling of the labeled macromolecular chain ends in solution. Line-width measurements on the spectra in Figures 3, 7, and 9 provide sufficient data to calculate a τ_c of 3.8 × 10^{-10} sec (±0.4 × 10^{-10}), a relatively small time for molecular motions in viscous media (see ref 5 for details of these types of calculations). The work of Tormala *et al.*[7] clearly shows the spectral changes accompanying the reduced degrees of freedom of a nitroxide with increasing molecular weight of a spin-labeled poly(ethylene glycol). In ranges of low τ_c values both the temperature and pressure[16] dependence of τ_c can be obtained.

Semiempirical correlations are also frequently employed to aid in spectral interpretations.[6,10] The most useful of these depends on recognizing that the separation between the outermost peaks of the derivative spectrum of a nitroxide label whose motion is relatively "frozen" can be identified as $2A_{zz}$, twice the principle component of the hyperfine interaction tensor parallel to the nitrogen π orbital.

Polyurethanes. The exact nature of the microstructure of polyurethane elastomers continues to be debated in spite of much investigative work and the long existing commercial pressures to exploit their properties (see ref 17-20 for additional citations). Generally, a rigid diisocyanate or a rigid diisocyanate-terminated segment is reacted with a flexible difunctional polyether or polyester to produce a solid having block-copolymer characteristics. Mechanical property, thermal, infrared, X-ray, nmr, spin probe, and other techniques have been focused on identifying the "micromorphology" of these materials. Cross-linking the polyurethane system *via* multifunctional additives or by using excess diisocyanate is easily achieved and produces networks of considerable interest.

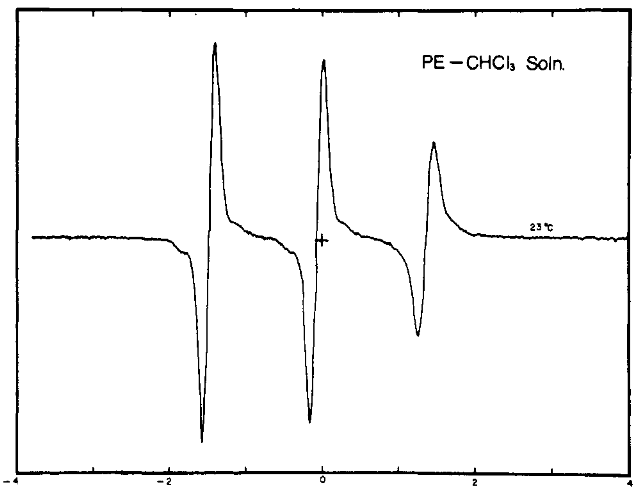

Figure 3. Esr spectrum of an end-labeled polyether in 20% $CHCl_3$ solution, in tens of gauss from H_0 = 3388.2 G, ν_0 = 9.535 GHz.

The basic idea of the present work was to produce a series of polyurethanes having different morphological character. These would be chemically bonded networks having pendant groups on the network chains to which spin labels could be attached.

Spin-Labeled Polyurethane Networks. As this first step in our studies of spin-labeled ntworks, the "hard block" of the polyurethane was kept as short as possible in one case, and in very high concentration in a second preparation. The first polymer was made by eliminating the usual chain extention step for the diisocyanate, *p,p'*-diphenylmethane diisocyanate (MDI), before reaction with a 2030 molecular weight polyether "soft segment" to produce a prepolymer. This was allowed to react with a cross-linking agent 1,1,1-trimethylolpropane (TMP). A very rubbery amorphous elastomer resulted having 20.4% (wt) MDI and designated MDI-PE-TMP. At the other extreme a polymer was made in which MDI was reacted with ethylene glycol and glycerin to produce a "hard block model" having 80% (wt) MDI. This second polyurethane was a hard amorphous solid at room temperature and is designated MDI-EG-GLY.

Stoichiometries were chosen so that chemically bonded networks would be produced with some pendant hydroxyls along the chains and at chain ends. Considering MDI-PE-TMP, an average molecular weight of the network chains of 2590 would result if every triol molecule completely reacted with the diisocyanate-terminated prepolymer. However, the typical structure shown in Figure 4, where the spin label has reacted with a TMP hydroxyl group in the center of a network chain, also existed. Statistically, ignoring side reactions, conditions were adjusted so that approximately 75% of the TMP in the final structure would be found in trifunctional network junction points, 22% existed in network chains as potential spin-label sites (one pendant hydroxyl), and 2% would be found at chain ends (also potential spin labels). It should be noted that the labeling position in this MDI-PE-TMP elastomer is always adjacent to at least one aromatic diisocyanate unit and usually adjacent to two. The spin labels when attached will then be at least 100 network chain atoms removed from a cross-link junction for this polymer.

The nitroxide derivative shown in Figure 2 was swollen into polymers from which the sol phase (~2%) was extracted. There it reacted with pendant hydroxyls to pro-

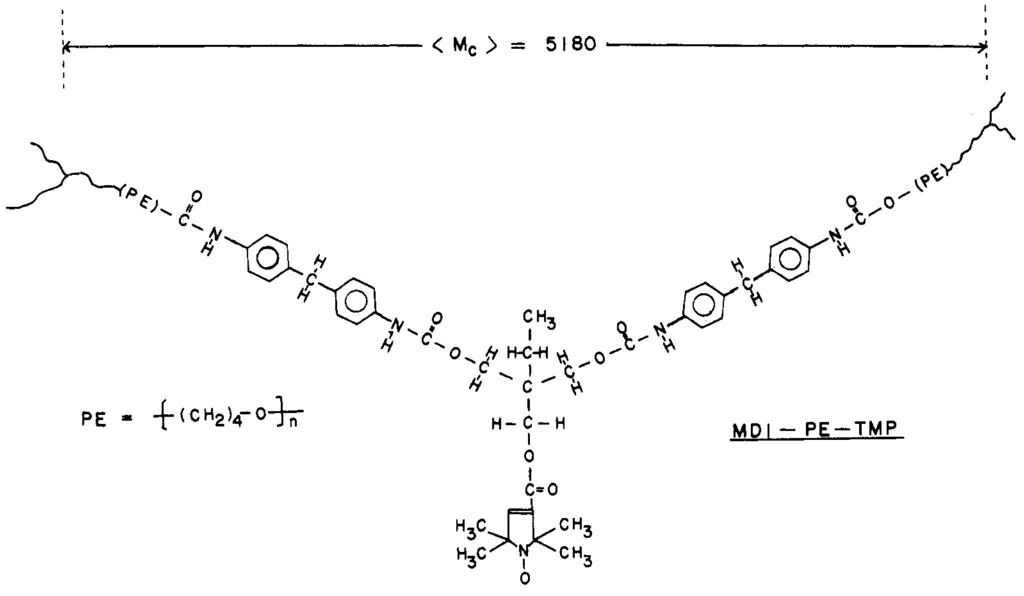

Figure 4. Representation of spin-labeled network chain. In the polyether (PE) segment $n \approx 28$.

duce the labeled networks. Unreacted spin label was later also extracted. Concentrations of less than 0.2 m*M* of spin label were used so exchange broadening of the esr spectrum was not present. Much less than 10% of the available hydroxyls were tagged with nitroxide.

Most of the experimental data reported in this paper were obtained on the polymer designated MDI-PE-TMP. Esr spectra of this spin-labeled network, and the same spin-labeled network swollen to equilibrium in chloroform, are presented below as functions of temperature. Also following are the spectra of this elastomer obtained as a strain was being applied to the network. The objective here was to establish correlations between moduli of elasticity, temperature, thermal history, and parameters derived from the esr analysis.

Each nitroxide in the final material experienced rotations and movements determined by the free volume and local morphology characterizing its immediate environment and by the thermal energy available. Each environment was in turn largely governed by the overall polyurethane composition since the spin-label concentration was so small. Thus, changes in microstructure of the labeled urethane with applied strain, or with increasing temperature, or with altered chemical composition will be reflected by esr spectral differences as the nitroxide responds to the triggering stimulus. To what extent one can expect a nitroxide spin label to perturb its environment is discussed by McConnell and McFarland.[10] With caution of interpretation, the esr spectra of spin-labeled networks should yield reliable and meaningful data on the "amorphous" solid's microscopic conditions.

Experimental Section

Spin Labels. The synthesis of 2,2,5,5-tetramethyl-3-pyrroline-1-oxyl was accomplished by a published method.[21] The starting material, 2,2,5,5-tetramethyl-3-pyrroline-3-carboxamide (Frinton laboratories), was oxidized with H_2O_2 followed by a reflux with aqueous sodium hydroxide. The resulting carboxylic acid radical was converted to the imidazole derivative (Figure 1) using 1,1′-carbonyldiimidazole in anhydrous chloroform solution.[22]

MDI-PE-TMP. Great precautions were taken to use dry, pure materials in the urethane syntheses in order to avoid urea and biuret group formations in the preparation.[23] Anhydrous conditions and clean starting materials are essential for reproducible results with polyurethanes. A prepolymer was made by reacting dried poly(tetramethylene oxide) of number-average molecular weight 2030 g/mol (determined as in ref 24) in the melt under anhydrous conditions with MDI. The isocyanate/hydroxyl molar ratio was 2.20. No catalyst was employed. Reaction conditions were 2 hr at 96°. The viscous prepolymer melt was mixed with enough TMP to provide an overall isocyanate/hydroxyl molar ratio of 0.95, degassed, and cured in stainless steel molds of 0.1-in. square section for 12 hr at 110°. The clear bubble-free product obtained was extracted extensively with a tetrahydrofuran-dimethylformamide mixture.

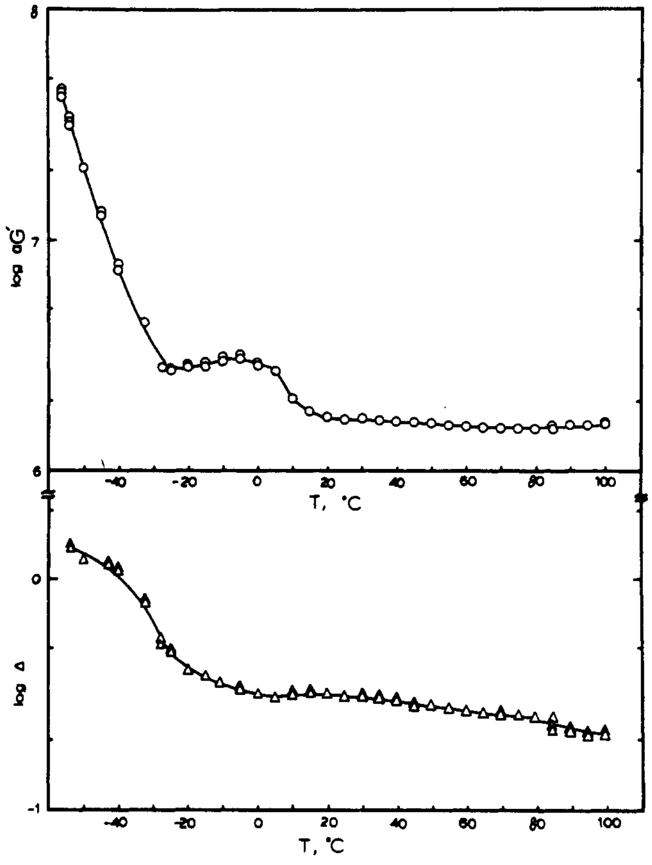

Figure 5. Relative shear modulus and damping of MDI-PE-TMP at various temperatures.

The spin label shown in Figure 1 was attached to the extracted network by swelling 2.647 g of polymer in chloroform and then adding 0.274 mmol of nitroxide. After 20 hr at 23° unreacted nitroxide was extracted and the sample was dried.

MDI-EG-GLY. In a dimethylacetamide solution MDI, ethylene glycol, and glycerin in the molar ratios of 1.03:0.90:0.10, re-

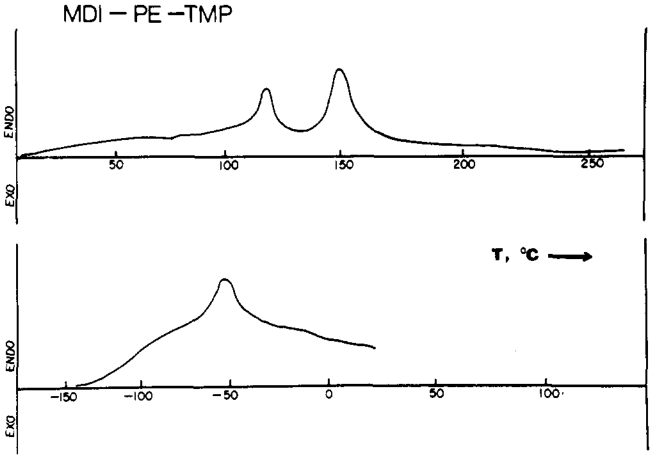

Figure 6. DTA of MDI-PE-TMP sample.

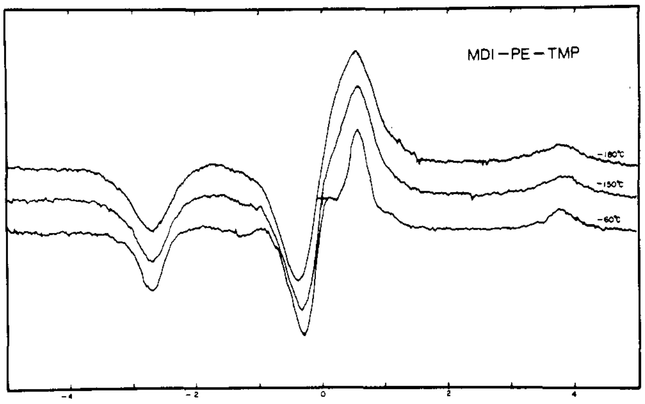

Figure 7. Esr spectrum of MDI-PE-TMP in tens of gauss from H_0 = 3296.6 G, ν_0 = 9.261 GHz.

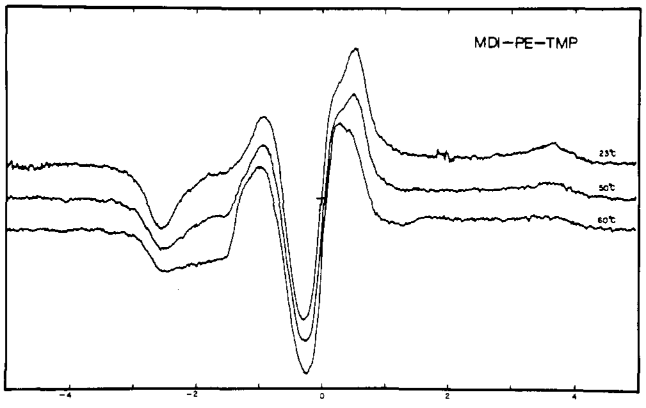

Figure 8. Esr spectrum of MDI-PE-TMP in tens of gauss from H_0 = 3298.6 G, ν_0 = 9.270 GHz.

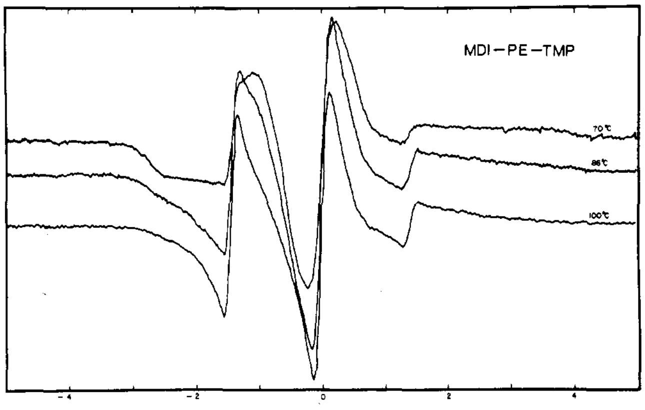

Figure 9. Esr spectrum of MDI-PE-TMP in tens of gauss from H_0 = 3299.0 G, ν_0 = 9.270 GHz.

spectively, were polymerized for 25 min at 115°. The resulting polymer was precipitated in distilled water and dried under vacuum.

The spin label was added to chloroform solution of the polymer of 23°. Unreacted nitroxide was extracted from the polymer.

Physical Measurements. Esr spectra were taken on a Varian E-12 x-band spectrometer. Spectra were completely reproducible; no power saturation or modulation amplitude effects were noted at the 0.9-mW and 0.8-G levels, respectively, of this study. Temperature control was to within ±1°.

Modulus-temperature data were obtained on a torsion pendulum at a nominal 30-Hz frequency. Torsional shear strains of less than 0.33 deg/in. were applied. Temperature equilibrations of 15 min were allowed. Data were obtained both by increasing and decreasing temperature profiles. Temperature was accurately known to ±0.1° in these measurements.

Stone-premco differential thermal analysis (DTA) equipment was used for the thermal measurements. Heating rates were 5°/min.

A special assembly was constructed which enabled the straining of elastomer samples while they were contained in the esr microwave cavity. Samples were end bonded to brass fixtures which attached at one end to a fixed point and at the other into a micrometer head. Extentions of several hundred per cent could be achieved with the design.

Results and Discussion

MDI-PE-TMP. The log decrement, log Δ, and a relative shear storage modulus, *aG′*, of this elastomer are shown in Figure 5 as functions of temperature. An uncertainty in cross-sectional area of the sample prevented an absolute calculation of *G′*, the real part of the complex modulus. A separate stress-strain determination however indicates that the rubbery plateau region between 20 and 100° lies at a Young's modulus of 2×10^7 dyn/cm^2. The low-temperature shapes of both mechanical behavior curves reveal large modulus and damping increases. This suggests a glass transition temperature, T_g, just below −60°.

Illinger, Schneider, and Karasz[25] have noted features resembling those of Figure 5 in the −20 to 0° range for a similar poly(ether urethane) of low MDI content (their sample 4). They felt that an observed peak in storage modulus between 0 and −50° was associated with crystallization of polyether segments which melted above room temperature. They concluded that a segregated domain structure was virtually absent in this composition of polymer. It is interesting to note that our curves in Figure 5 contain points obtained on both increasing and decreasing temperature. No apparent mechanical property differences exist based on this thermal cycling.

A T_g of MDI-PE-TMP clearly shows in the DTA data (Figure 6) at −55°. This is probably the network restricted T_g that the polyether homopolymer experiences at about −88°.[25] Other endotherms are prominent at 119 and 150°. The nature of these higher temperature transitions is not settled.[17,20] Thermal history of the sample is known to be important in the elevated temperature peak locations. It is worthwhile to note the occurrence of these endotherms in our sample of such low "hard-block" content.

Esr spectra of MDI-PE-TMP over a −180 to 100° range appear in Figures 7, 8, and 9. The abscissa is in tens of gauss variation from the central field location indicated in the caption as H_0 and frequency ν_0.

The immobilized nitroxide radical spectrum at −180° shows characteristically broad outer extrema and a large single central peak in these derivative curves. The outer extrema (minimum on left to maximum on right) are separated by 64.6 G or 181.6 MHz. As temperature was raised

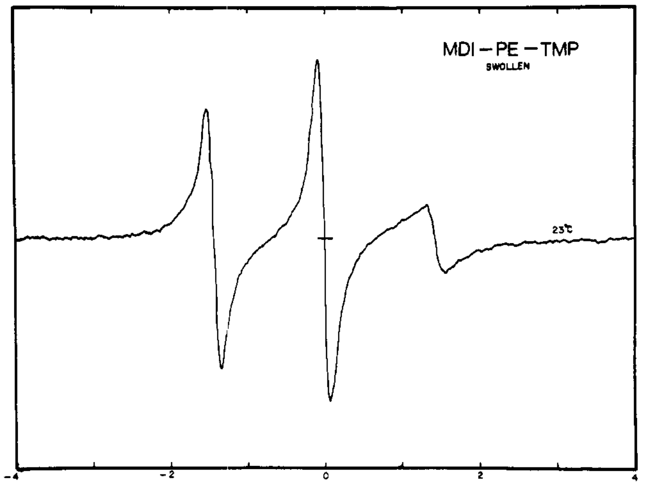

Figure 10. Esr spectrum of MDI-PE-TMP swollen in $CHCl_3$. Deviations from H_0 = 3298 1 G, ν_0 = 9.269 GHz given in tens of guass.

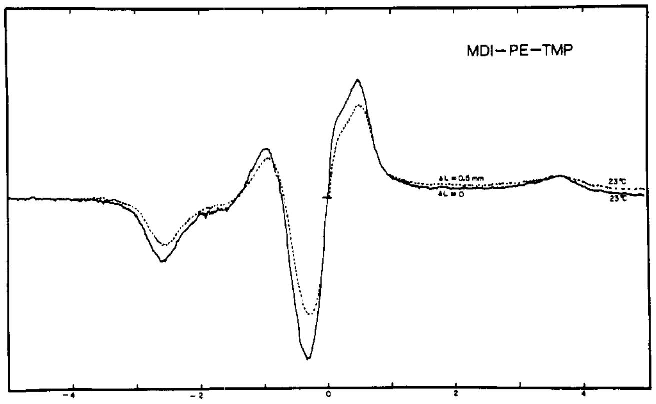

Figure 11. Esr spectrum of MDI-PE-TMP in an unstrained (solid line) and strained (α = 1.5) state.

these outer extremes migrate centrally, going through a very broad region (60° curve, Figure 8) where it appears that a distribution of extrema exists. At 86° and, clearly, at 100° (Figure 9) the spectra indicate rapid motion of the spin label although slower than that shown in Figure 3. That being the case, the 100° spectrum yields an isotropic (average) hyperfine splitting constant, a_N, of 14.4 G, and theoretically[1,5] a τ_c of 2.45 × 10^{-9} sec (±0.25 × 10^{-9} sec) at 100° was calculated.

Samples of spin-labeled MDI-PE-TMP network were swollen to equilibrium at room temperature in chloroform. The effect of this drastic change in morphology on the esr spectrum is illustrated in Figure 10. Comparison to the 23° spectrum of Figure 8 shows that the nitroxide has much more motional freedom in the swollen state. In fact the 100° spectrum of dry elastomer quite closely resembles the 23° spectrum of swollen elastomer. However, the latter has a rotational correlation time of 1.4 × 10^{-9} sec (±0.20 × 10^{-9} sec), a factor of about 2 faster than the τ_c of the former.[26] Below −40° the swollen sample's spectrum indicated highly restricted nitroxide motion.

Using the special esr sample holder described above a number of spectra were obtained on MDI-PE-TMP specimens held in an equilibrium state of tensile strain. Extention ratios, $\alpha = L/L_0$, up to 1.7 were applied at 23° and obtained up to α = 1.2 at elevated temperatures. No large spectral changes could be induced by these conditions. Figure 11 shows a typical result. Only the attenuation of signal intensity due to lowering of the detectable radical population on straining was apparent. Experimental difficulties presented larger strains and temperature ranges from being employed at this point.

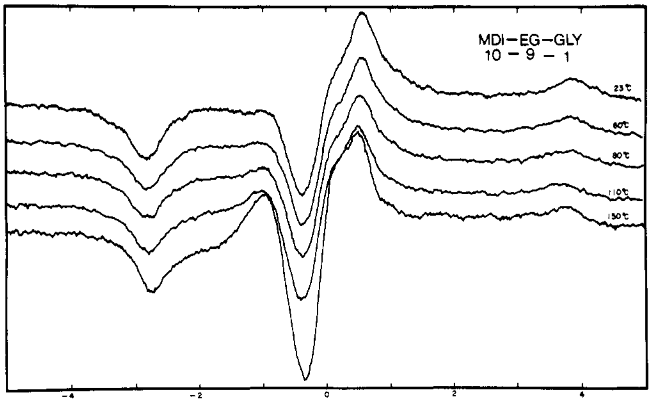

Figure 12. Esr spectrum of MDI-EG-GLY at various temperatures. Deviations from H_0 = 3300.2 G, ν_0 = 9.170 GHz are in tens of gauss.

MDI-EG-GLY. This polymer was prepared by a method reported to produce a completely amorphous solid.[27] Powder pattern X-ray diffraction spectra were run on MDI-EG-GLY and only amorphous halos with no sharp edges or spots were observed. No endotherm peaks were detected by DTA measurements between −50 and 150°.

A crushed powder of the spin-labeled polymer was placed in a standard esr tube. The spectra obtained at various temperatures are shown in Figure 12. Obviously the sample morphology (as reflected by the nitroxide motion) is maintained throughout the 23-150° span and provides a very hindering local environment for molecular motion. The outer extrema are separated by 66.23 ± 0.75 G for each spectrum shown in Figure 12.

Summary and Conclusions

In this work a bracketing of segmented polyurethane behavior as monitored by spin-label motion was attempted as a prelude to further investigations. Nitroxide radicals were successfully attached to such polymers. Reproducible (over more than a 3-month period) esr spectra which differed according to chemical composition, diluent content, and temperature were produced. A MDI-PE-TMP material of low "hard block" content showed no esr spectral changes with moderate applied strains over a 72° variation in temperature. Swelling of this elastomer shifted the onset of "rapid rotation" of the nitroxide at least 50° lower in temperature. The opposite end of the bracket was provided by the sample MDI-EG-GLY. It had a very high MDI content. No occurrence of rapid rotation was detected up to 150° in this polymer.

Figure 13 aids the esr spectral interpretation. The outer extrema separations, designated $2A_{zz}$, in gauss have been plotted for each sample. Where the outer peaks were broad, *e.g.*, 60° spectrum of Figure 8, the extremum location was approximated as the midpoint of the base line to base line values of that peak. Dramatic increases in nitroxide motion are indicated on heating through certain temperature ranges (these may be sharper given more data) for both of the MDI-PE-TMP samples, but not at all for the MDI-EG-GLY. Using Rabold's type of transition temperature definition,[4] T_w's of −10 and 70° are calculated for the swollen and dry elastomeric sample, respectively. T_w was the temperature at the midpoint between extrema separations for "frozen" and "freely rotating" nitroxides. Approximately 80° separate the two sigmodial-shaped curves, and both values of $2A_{zz}$ actually approached $2a_N$ with increasing temperature. This $2a_N$

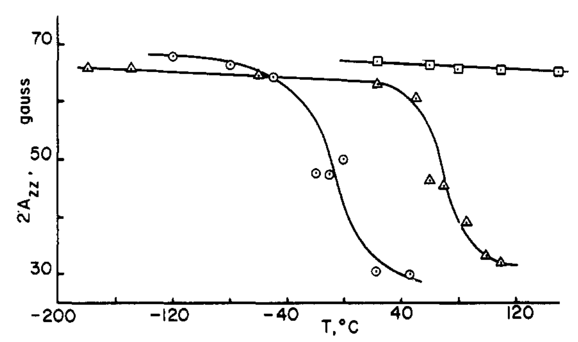

Figure 13. Separation of outer extrema of the esr spectra of MDI-PE-TMP (▲), MDI-EG-GLY (⊡), and swollen MDI-PE-TMP samples (⊙).

asymptote was very close to 31.8 G, a value determined from Figure 2 for free nitroxide in solution. Thus a flexibly structured cage was experienced by nitroxides above 120° for the MDI-PE-TMP, above 23° when the same polymer is swollen, but not below 150° for MDI-EG-GLY.

The spin label was noted to be always adjacent to MDI units in the MDI-EG-GLY polymer. One would expect the spin label to produce spectra indicating the changing participation of these MDI units in microdomains with altering macroscopic states. Even with the perturbation of the bulky nitroxide the strongly cooperative interactions of such a solid and the very low spin concentrations suggest that the observed transitions in Figure 12 are associated with a physical phenomena of the unlabeled polymer. A key point to be made is the absence of any esr spectral changes in the MDI-PE-TMP lower than 70°. This must be contrasted with the mechanical and thermal data which show changes, but ones associated with the soft poly(ether) segment. It is tempting to associate this elastomer transition at 70° with the DTA peak at 119° based on T_w to T_g and to melting temperature correlations found in ref 4. Because of the statistical distribution of labels and the necessarily heterogeneous character of polymeric microdomains the width of the transition can be rationalized. Exact identification of the transitions reported in this study depends on further work. It is sufficient to note here the indications of transitions in an amorphous polyether urethane having a very low "hard segment" composition.

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Theoretical Analysis of Pyrrolidine Ring Puckering and the Conformational Energies of Proline and 5-Methylproline Dimers[1]

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ABSTRACT: The stable geometries of the pyrrolidine ring are obtained from semiempirical energy calculations. The puckering of the ring is studied as a function of the dihedral angle θ associated with the atoms C$^\delta$, N, C$^\alpha$, and C$^\beta$. For an isolated prolyl ring, for each value of θ, two energy minima are observed corresponding to two positions of the C$^\gamma$ atom. While the global energy minimum occurs at $\theta = -10°$, it is found that θ can vary from -20 to $+20°$ within 0.5 kcal/mol from the minimum energy. The effect of this flexibility on the conformational characteristics of an internal Pro-Pro dimer is studied by calculating the conformational energies of the dimer. It is shown that while trans dimer prefers γ^+ and γ^- puckered rings, the cis dimer prefers β^+ and γ^- puckered rings. These studies are extended to the case of 5-methylproline dimers.

Several theoretical studies on the conformational stability of polyproline and peptides containing proline have been reported.[2-7] In many of these, the pyrrolidine ring itself has been kept rigid either in a planar structure or in a puckered conformation. Accordingly, in these studies, the torsion angle φ^8 about the bond N–C$^\alpha$ was kept constant at a suitable value to ensure ring closure. Recently, however, it is becoming evident that the puckering of the pro-