observation in atactic polystyrene can now be related to the much faster excimer formation of the meso sequences as compared to the racemic ones. Values of rate constants or activation energies obtained for atactic polymers hence only reflect polymer composition.

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Mechanochemical Effects in a Poly(α-amino acid)

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ABSTRACT: The relationship between chain conformation and the physical and mechanical properties of a poly(α-amino acid) has been investigated. In order to eliminate intermolecular effects, cross-linked polymers were prepared and the properties investigated in the swollen state. In water, films of poly[(2-hydroxyethyl)-L-glutamine] take the random coil conformation and the mechanical behavior is elastomeric. In methanol, the chains are α-helical and plastic deformation is observed. The helical content was varied by using water-methanol mixtures and by increasing the number of methylene groups in the side chain. Elastomeric behavior was observed in the coil-to-helix transition region. This was interpreted in terms of the high chain flexibility of the interrupted helix.

Introduction

The relationship of individual chain characteristics such as conformation and mobility to the physical and mechanical properties of the condensed state is of fundamental importance. Only rarely, as in the case of rubber elasticity, has a quantitative theory been developed which successfully describes this relationship. In general, the effects of molecular properties and supermolecular or morphological features are difficult to separate.

The poly(α-amino acids) can provide new insight into this important area. These polymers exhibit chain conformations which have been well characterized in solution and the solid state. Poly(L-glutamic acid) and poly(L-lysine) have been lightly cross-linked with glycerol and formaldehyde, respectively.[1,2] Reversible dimensional changes of the water-swollen network were observed to accompany the pH-induced helix-to-coil transition.

The helix-to-coil transition has been described in terms of the interrupted helix model. As the helical content decreases from unity and the fraction of randomly coiled residues increases, the entire chain segment can no longer be a rigid rod but becomes flexible at the points where the randomly coiled residues interrupt the helical sections. The shape of such a chain segment may be pictured as a broken rod which consists of rigid rods connected by short flexible joints.

Experimental support for the interrupted helix as the predominant molecular structure in the region of the helix-to-coil transition is provided by measurements of size-dependent properties such as limiting viscosity number and the radius of gyration. Okita et al.[3] found that the limiting viscosity of poly[(3-hydroxypropyl)-L-glutamine] in water-methanol mixtures increased gradually with increasing helicity until a helix content of about 75% was reached; then the viscosity showed a sharp rise. Miyake et al.[4] observed a broad minimum followed by a sharp rise in the curve of intrinsic viscosity vs. helical fraction for a high molecular weight sample of poly[(2-hydroxyethyl)-L-glutamine] in 2-propanol-water mixtures. Ohta et al.[5] observed that the mean-square radius of gyration showed the same dependence on helicity as the viscosity for this system.

The viscosity vs. helicity curves have features quite similar to the theoretical curves for the molecular dimensions vs. helicity first presented by Nagai[6] and later by Miller and Flory.[7] This suggests a close relationship between the intrinsic viscosity and the molecular dimensions of interrupted helices. The minimum has also been pre-

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dicted by both Nagai and Miller and Flory. Their calculations predict that the average dimension of a low molecular weight sequence in the random coil conformation exceeds that for the α helix. Hence the polymer chain shrinks with the appearance of short helical sections.

The backbone and segmental mobility of the polymer are expected to be well correlated with the NMR spin-lattice relaxation time. Saito and Smith[8] observed that titration curves of ^{13}C chemical shifts of poly(L-lysine) were very similar to that of the specific rotation vs. pH, with gradual changes between 9 and 11, while the relaxation time was seen to decrease sharply at pH 10.2. They also observed no changes in the relaxation time of poly(L-lysine) oligomers in going from the random coil to the α helix. This suggests that in the region of the coil-to-helix transition the chains have considerable segmental mobility due to the flexibility of the random coil regions.

In order to examine the mechanochemical effects of the helix–coil transition, cross-linked films of the poly[(ω-hydroxyalkyl)-L-glutamines] have been prepared. The (ω-hydroxyalkyl)-L-glutamine polymers are nonionizable, water-soluble poly(α-amino acids) whose conformation depends on various factors including the length of the side chain, molecular weight, temperature, and solvent.[9,10] In water, poly[(2-hydroxyethyl)-L-glutamine] takes the random coil conformation and in methanol the α-helical conformation. Alternatively, increasing the number of methylene groups in the side chain results in an increase in the helical content in aqueous solution. The properties of the cross-linked films were studied in the swollen state to facilitate changes in conformation and to minimize intermolecular effects.[11] This paper describes the preparation of the cross-linked network and the mechanochemical phenomena associated with the helix-to-coil transition.

Experimental Section

Materials. Poly(γ-benzyl L-glutamate) (PBLG) was prepared by polymerization of the N-carboxyanhydride of γ-benzyl L-glutamate in methylene chloride–benzene solution.[12] Polymer prepared with triethylamine as the initiator had a viscosity-average molecular weight of about 250 000.[13] Lower molecular weight polymer was prepared with n-hexylamine as the initiator. The viscosity-average molecular weight was about 44 000.

Films of PBLG were prepared by casting a 1% by weight solution of the polymer in either benzene, dioxane, or chloroform on glass plates. The casting was repeated as necessary to achieve the desired thickness. Films were dried under vacuum for 3–4 days at 30–40 °C.

The films of PBLG were converted to the ω-hydroxy glutamine and cross-linked in a single step. Films were immersed in a solution of the ω-hydroxy amine and the diamine cross-linker at 55 °C. The ω-hydroxy amines were distilled under vacuum over barium oxide, and 1,12-dodecyldiamine was dried under vacuum.

In one series of experiments, the reaction time was varied from 2 h to 6 days. Films for physical and mechanical characterization were reacted for 4 h. The films were washed with ethanol and methanol and equilibrated in water, methanol, or water–methanol mixtures as desired without drying. Alternatively, films were stored in methanol at 10 °C until used.

Linear PHEG was prepared by the same procedure with the cross-linker omitted. The viscosity-average molecular weight was about 30 000.

Swelling Measurements. The swelling was determined by equilibrating film specimens in water, methanol, or a water–methanol mixture at room temperature. When a constant weight was achieved, the specimen was removed, blotted to remove surface liquid, and weighed. The specimen was then dried in a vacuum oven. The swelling ratio q is defined as the ratio of the wet weight to the dry weight.

Circular Dichroism Spectroscopy. The CD spectra were recorded at 20 °C in the 200–260-nm range with a Jasco J-20 recording spectrometer. Measurements on swollen films were made with the specimen sandwiched between quartz plates to prevent evaporation of the solvent.

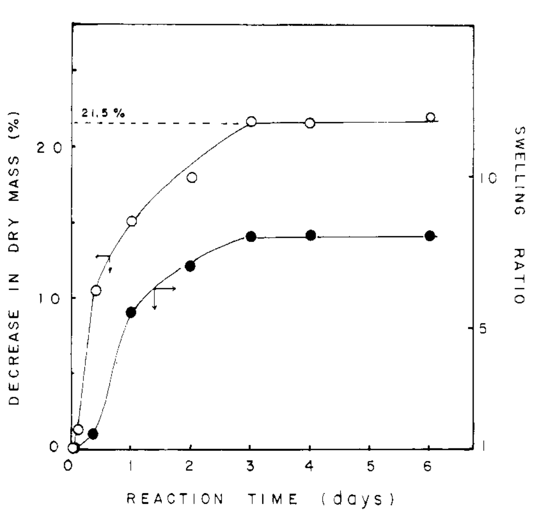

Figure 1. Change in dry mass and swelling ratio during the exchange reaction (100-μm PBLG films, 2.44 mol % cross-linker).

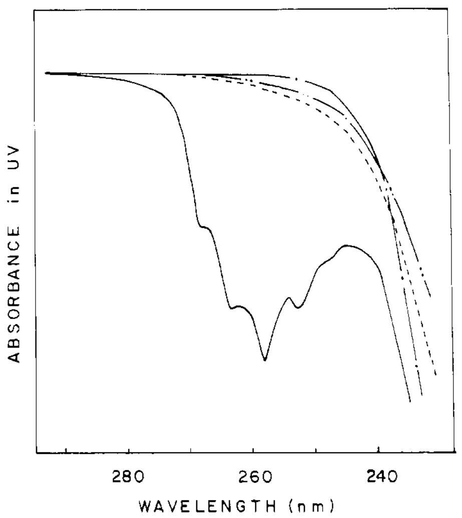

Figure 2. UV spectra of PBLG and cross-linked poly[(ω-hydroxyalkyl)-L-glutamine] films: (——) PBLG; (–·–) PHEG; (–··) PHPG; (-·-·) PHPeG.

Stress–Strain Measurements. The mechanical properties were determined with the film specimen immersed in water, methanol, or a water–methanol mixture at room temperature. An Instron tester was used with a strain rate of 25%/min. The specimen geometry was ASTM Micro-tensile with a width of 0.5 cm and a gauge length of 2.0 cm.

Results

Film Preparation. The exchange reaction was followed by the change in dry mass of the film and the swelling ratio in water. Figure 1 shows the decrease in dry mass due to the exchange of the benzyl groups for hydroxy amine groups. When reaction is complete, at about 4 days, the weight loss approaches the theoretical value (21.5%) for the complete conversion of PBLG to PHEG. Figure 1 also shows the increase in hydrophilicity, as indicated by the increase in swelling ratio in water, which accompanies the exchange reaction.

The complete reaction is demonstrated by UV and IR analysis. No detectable absorption due to benzyl groups is observed at 257 nm in the UV spectra of the reacted films (Figure 2). The complete exchange of the benzyl groups is also shown by the disappearance of IR absorption peaks at 1750 and 1450 cm^{-1}.

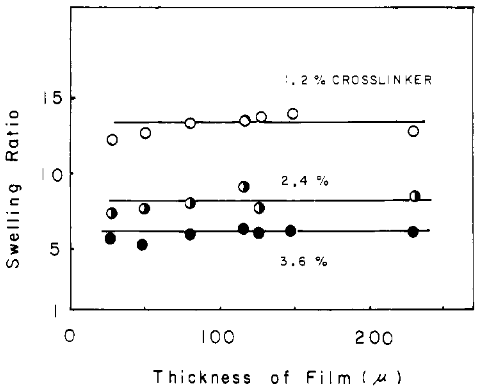

Figure 3. Effect of initial PBLG film thickness on the swelling ratio in water of the final cross-linked PHEG film.

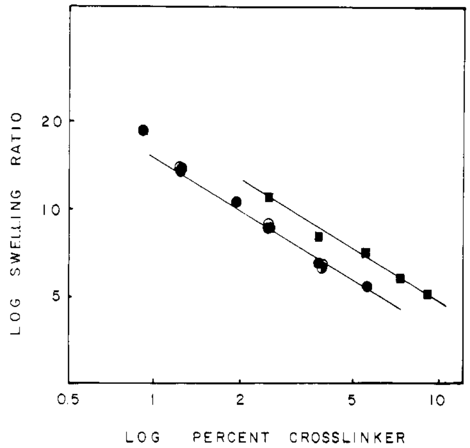

Figure 4. Log–log dependence of the swelling ratio in water on the mole percent cross-linker in the reaction. Films were prepared from high molecular weight PBLG cast from chloroform (○), dioxane (◑), and benzene (●), and low molecular weight PBLG cast from benzene (■).

Cross-linked films were prepared from PBLG films which varied in initial film thickness from 20 to 250 μm. Figure 3 shows the effect of film thickness on the swelling ratio of the cross-linked films prepared with three different cross-linker concentrations. The initial film thickness has no significant effect on the swelling ratio, which is strong evidence that the cross-linking produced by the heterogeneous cross-linking reaction occurs uniformly through the thickness of the film.

The effect of cross-linker concentration in the reaction on the swelling ratio of the cross-linked film in water is shown in Figure 4. The dependence of the volume swelling ratio, Q, on the number of repeat units between cross-links, n_c, for highly swollen networks is given by rubber elasticity theory[14] according to

$$Q^{5/3} = (M_0 n_c/V)(\tfrac{1}{2} - \chi)(1 - 2M_c/M) \qquad (1)$$

where M_0 is the molecular weight of the repeat unit, V is the molar volume of solvent, and χ is the interaction parameter. The swelling ratio by weight, q, is assumed to be proportional to Q and is plotted as a function of the percent cross-linker in Figure 4. Since the observed slope of $-^3/_5$ in Figure 4 is that predicted by eq 1, it appears that the effective cross-link density (n_c^{-1}) is proportional to the percent cross-linker in the reaction. Figure 4 also shows that the morphology of the initial PBLG film, which was varied by casting from different solvents, has no effect on the swelling ratio.

Swelling ratios of films prepared from PBLG of two different molecular weights are compared in Figure 4. The functional dependence on cross-linker concentration is the same for both molecular weights (slope $-^3/_5$) but the data for the lower molecular weight PBLG are shifted to higher swelling ratios. This difference can be attributed to network imperfections resulting from chain ends and is accounted for by the term $1 - 2M_c/M$ in eq 1.

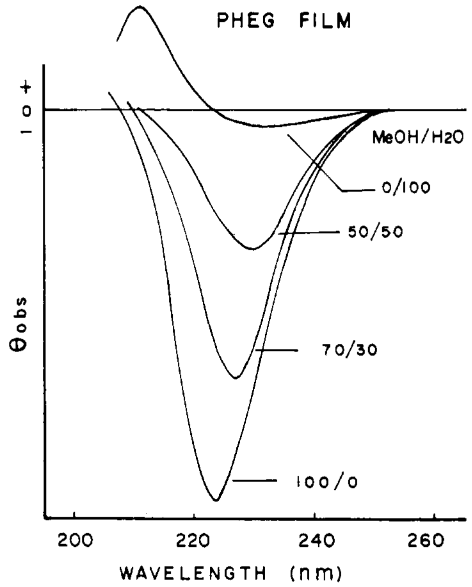

Figure 5. Circular dichroism spectra of cross-linked PHEG films in water–methanol mixtures.

Helix–Coil Transition. The chain conformation in the swollen state was characterized by circular dichroism spectroscopy (Figure 5). In water, cross-linked PHEG films exhibit a weak negative peak at 235 nm and a positive peak at about 216 nm. This spectrum is characteristic of the random coil conformation. In methanol, the cross-linked PHEG film has a strong negative peak at 223 nm. The α-helical conformation is usually characterized by two negative peaks: the broad n–π^* transition at about 223 nm and the π–π^* transition at 209 nm. For linear PHEG the π–π^* transition appears as a shoulder on the broad n–π^* peak, but for the cross-linked films the π–π^* transition could not be resolved.

Quantitative interpretation of solid-state CD spectra is not possible because of uncertainties in precise film thickness. Relative changes in conformation were obtained by comparing spectra of the same film in different solvents. The helical content was estimated from the depth of the peak at 223 nm, and the helical content relative to that in methanol is shown in Figure 6. Data for both solutions of linear PHEG and swollen films of cross-linked PHEG are compared. The data for the two systems superimpose, and the S-shaped curve shows the helix-to-coil transition at a water–methanol ratio of about 40–60.

Data for cross-linked films prepared from hydroxy amines with 3, 4, and 5 methylene groups are included in Figure 6. The effect of increasing the length of the side chain is an increase in the amount of α helix. Thus the helix-to-coil transition for PHPG occurs at a water–methanol ratio of about 75–25 while PHBG and PHPeG are essentially α helical at all water–methanol ratios. This increased stability of the α helix as the side chain is made more hydrophobic has been observed previously for solutions of the linear polymers.[10]

The swelling ratios of cross-linked films in water–methanol mixtures are shown in Figure 7. The swelling ratio of PHEG and PHPG films decreases as the helicity increases. The swelling curves show a broad transition, with the midpoint in the swelling change at a water–methanol composition close to that of the CD curves. The

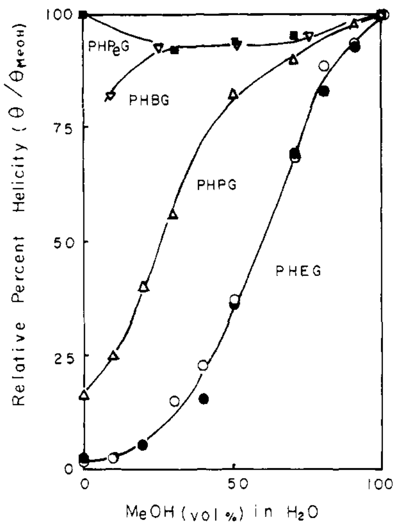

Figure 6. Relative percent helicity of cross-linked poly[(ω-hydroxyalkyl)-L-glutamine] films in water-methanol mixtures. Data for linear PHEG (●) are also included.

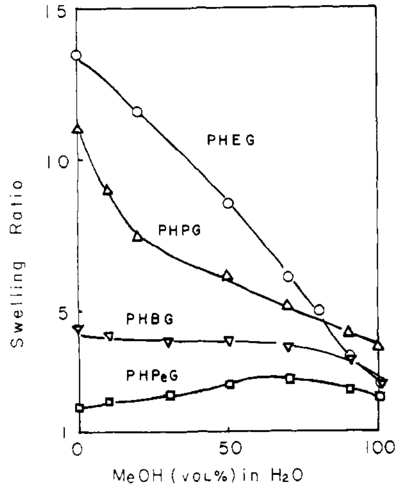

Figure 7. Swelling ratio of cross-linked poly[(ω-hydroxyalkyl)-L-glutamine] films in water-methanol mixtures.

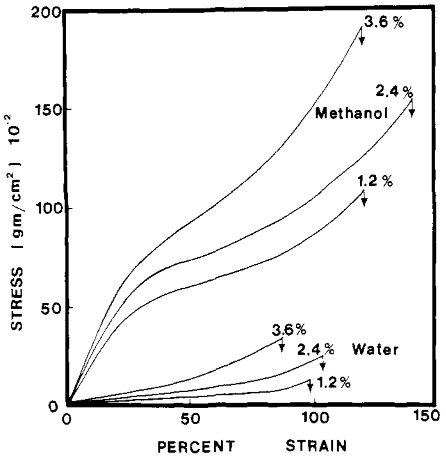

Figure 8. Stress-strain curves of PHEG (1.2, 2.4, and 3.6% cross-linker) in water and methanol.

films of PHBG and PHPeG, which are essentially α helical at all water-methanol ratios, show no solvent-dependent changes in the swelling ratio.

Mechanochemical Effects. The mechanical behavior of water-swollen films of PHEG where the chains are in the random coil conformation is typical of a cross-linked elastomer. The stress-strain curve (Figure 8) is independent of strain rate and completely reversible, and no stress relaxation at constant elongation is observed.

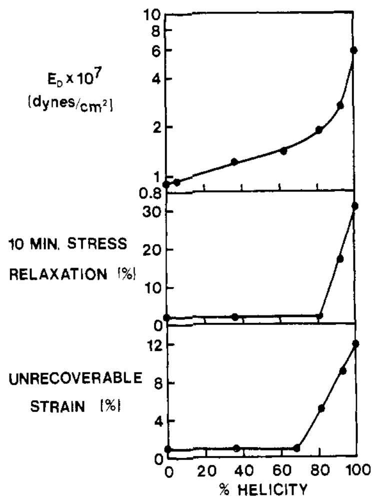

Figure 9. Change in various mechanical parameters for cross-linked PHEG films as a function of the percent helicity.

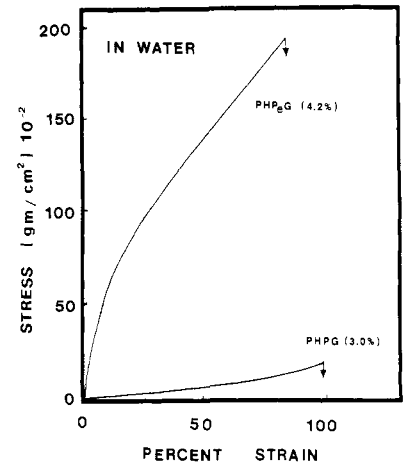

Figure 10. Stress-strain curves of PHPG (3.0% cross-linker) and PHPeG (4.2% cross-linker) in water.

The methanol-swollen films are α helical and exhibit a sigmoidal stress-strain curve. The modulus calculated from the initial slope is almost an order of magnitude higher than in water. The mechanical behavior in methanol is characteristic of plastic deformation in that the stress-strain curve is strain-rate dependent, stress relaxation is observed at constant strain, and at high elongation permanent set occurs.

The mechanical behavior in the coil-to-helix transition region was determined by testing films in various water-methanol mixtures. The helical fraction at each water-methanol composition was obtained from the CD curves. The mechanical parameters are plotted as a function of helical fraction in Figure 9. The modulus shows a gradual increase with increasing helicity followed by a sharp increase as the helical fraction approaches unity. The transition in deformation mechanism from elastic to plastic is indicated by the recovery and stress-relaxation curves. Both parameters show that the behavior remains elastomeric as the helical fraction increases up to 0.70. Then an abrupt increase in the plastic component of the deformation is observed.

The mechanochemical effect can also be observed by comparing the mechanical behavior of PHPG and PHPeG in water (Figure 10). The PHPG film has some α-helical content but exhibits qualitatively the same elastomeric behavior as PHEG. On the other hand, PHPeG is in the α-helical conformation in water and the stress–strain curve resembles that of α-helical PHEG in methanol.

Discussion

A fundamental investigation of mechanochemical phenomena in the swollen state depends on the preparation of a well-characterized polymer network. In the present study a method has been developed for the preparation of cross-linked poly[(ω-hydroxyalkyl)-L-glutamines] by the heterogeneous, competition reaction of the ω-hydroxyalkyl amine and an alkyl diamine cross-linker on films of poly(γ-benzyl L-glutamate). Films prepared by this method are highly reproducible in terms of their physical and mechanical properties. It has been shown that exchange of the benzyl groups is complete and that reaction of the cross-linker occurs uniformly through the film thickness. The initial morphology of the PBLG film is apparently destroyed in the cross-linking reaction since the method used to prepare the initial PBLG film has no measurable effect on the properties of the final product.

It has been shown that the cross-link density is proportional to the concentration of cross-linker in the hydroxy amine–diamine reaction mixture. The precise cross-link density has not been determined because of uncertainty in the relative reactivities of hydroxy amine and diamine and also because estimation of the fraction of reacted diamine molecules which forms effective cross-links is difficult. The length of the chain segment between cross-links has been previously estimated from combined swelling and stress–strain data.[11] Values obtained by this method were larger than the values predicted from the composition of the reaction mixture by a factor of 4.

The conformation of poly[(ω-hydroxyalkyl)-L-glutamines] in solution has been well characterized by CD and ORD. The conformation of these nonionizable, water-soluble poly(α-amino acids) depends on various factors, including the solvent and the number of methylene groups in the side chain. Although quantitative interpretation of solid-state CD spectra is not possible due to uncertainties in film thickness, it has been demonstrated that the shape of the CD curve which characterizes each conformation is essentially the same for solution and solid-state spectra.[15,16] The CD spectra of swollen poly[(2-hydroxyethyl)-L-glutamine] networks show that in water the chain segments take the random coil conformation while in methanol they are α helical. The relative helical content of the swollen cross-linked films shows the same dependence on the solvent composition in water–methanol mixtures as solutions of the linear polymer. In both cases the helix-to-coil transition is observed at a water–methanol ratio of about 40–60. The increase in α-helical content of water-swollen films as the number of methylene groups in the side chain is increased also parallels the observed behavior of aqueous solutions of the linear polymers. It appears that the presence of network junctions does not affect the conformational properties of the chain segments, and the latter are long enough to take the same conformation as a free chain in solution.

The mechanical response of the swollen network varies markedly from elastic behavior in water to plastic deformation in methanol. The change in deformation mechanism can be attributed to the difference in chain conformation. In water, the chain is in the highly flexible random coil conformation. As a result the behavior is typical of an elastomer, with the predicted relationship between swelling ratio and cross-link density, the low modulus, and the reversible, time-independent mechanical response. The α-helical conformation is stabilized by intramolecular hydrogen bonds and in this conformation the chain is much more rigid than in the random coil. Unlike the random coil, the rigid α helix does not deform elastically as indicated by time-dependent, irreversible deformation behavior. It was previously demonstrated with polarized infrared measurements that under stress some of the α-helical chains are converted to the β-sheet conformation.[11] The β-sheet chains are well oriented in the direction of stress. The conversion from α helix to β sheet is irreversible and probably accounts for the nonrecoverable deformation of the α helix.

The transition from elastic to plastic behavior does not parallel the coil-to-helix transition. Rather the formation of α helix does not affect the deformation mechanism until the helical fraction is about 0.70. Then an abrupt transition from elastic to plastic behavior is observed. Deformation of the different poly[(ω-hydroxyalkyl)glutamines] in water shows qualitatively the same phenomena in that PHPG, which is partially helical, shows elastic behavior similar to PHEG and only PHPeG, which is essentially completely helical in water, deforms like helical PHEG in methanol.

These observations are interpreted in terms of the interrupted helix. The abrupt change in deformation mechanism with helicity parallels the changes in molecular dimensions[3–5] and segmental mobility.[8] A primary molecular requirement for elastomeric behavior is that the chain segments between cross-links be coiled rather than extended and highly flexible. Elastomeric behavior in the transition region can be attributed to the interrupted helix conformation, where interruptions of the helical sections by randomly coiled residues occur sufficiently frequently to impart overall flexibility to the chain segments between cross-links.

The gradual increase in the modulus with increasing helicity in the elastic region is attributed to shortening of the "effective" chain length between cross-links caused by formation of helical sections and consequently a decrease in the number of flexible bonds. As the helical fraction approaches unity the modulus represents the rigid rod and increases rapidly.

The swelling behavior does not change abruptly in the transition region. The swelling curves are similar to that of specific rotation, with a gradual change as the solvent composition is varied. The present interpretation is that the swelling is determined less by the molecular dimensions than by interactions with the solvent. A similar explanation has been suggested for the gradual change in ^{13}C NMR chemical shift accompanying the helix–coil transition of poly(L-lysine).[8]

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Hydrogen-Bonding Properties of Hard-Segment Model Compounds in Polyurethane Block Copolymers

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ABSTRACT: The N–H stretching vibration in three model hard-segment compounds for polyurethane block copolymers based on 2,4- and 2,6-toluene diisocyanate (TDI) and *p,p*′-diphenylmethane diisocyanate (MDI) with 1,4-butanediol has been studied by infrared spectroscopy. Changes in the frequency, half-width, and integrated intensity resulting from thermal treatment have been correlated to the degree of structural organization as evidenced by differential scanning calorimetry (DSC). The temperature dependence of hydrogen bonding in these materials was also investigated.

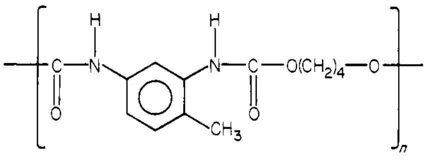
Introduction

Segmented polyurethanes are a class of materials consisting of alternating hard- and soft-segment units. The hard segments are commonly based on *p,p*′-diphenylmethane diisocyanate (MDI), 2,6- or 2,4-toluene diisocyanate (TDI), and butanediol (BD) whereas the soft segments are typically low molecular weight polyesters or polyethers. Segregation of the hard-segment units into domains is believed to be responsible for their unusual properties (i.e., enhanced modulus, high extensibility, and resiliency) and morphologies.[1–3]

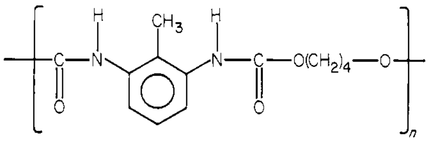
Such polyurethanes are extensively hydrogen bonded. In all cases, the N–H group of the urethane serves as the proton donor while the acceptor group may include the carbonyl and adjacent oxygen atom in the urethane group as well as the ester carbonyl or ether oxygen of the soft segment. Although hydrogen bonding is an important structural feature of segmented polyurethanes, its influence on their properties and morphologies is not clear. Working on a series of MDI-based polyurethanes, Cooper et al.[4] have concluded that the thermal behavior of hydrogen bonding is independent of morphology and depends primarily on the glass transition temperature of the hard segments. Investigations by the X-ray diffraction method[5,6] of hydrogen bonding and the orientation mechanisms of segmented polyurethanes have suggested otherwise; both crystallization of the hard segments and the observed orientation behavior have been explained by "restructuring" of the physical cross-linking caused by hydrogen bonding.

While hydrogen bonding in segmented polyurethanes has been the subject of numerous investigations using infrared spectroscopy, very little systematic interpretation has so far been made of the spectral features associated with the N–H absorption band. As in most hydrogen-bonded systems, this stretching mode displays well-known and characteristic perturbations: frequency shift, increase in bandwidth relative to the natural width, and enhancement of intensity. The frequency shift has been generally accepted as a measure of the strength of the hydrogen bond, correlating well to hydrogen bond energy[7] and NH---O distance in solids.[7–10] Although the origin of the latter two effects is less clear, changes in these properties are no doubt indicative of the structural and hydrogen-bonding features of these systems and may therefore lead to additional information about the effects of hydrogen bonding on morphology.

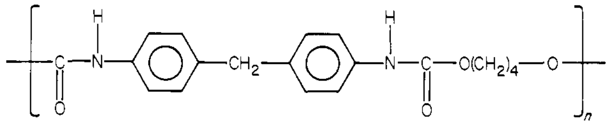
Chart I



2,4-TDI-BD



2,6-TDI-BD



MDI-BD

The present work is concerned with a detailed analysis of the N–H stretching vibration in three copolymers based on MDI, 2,6-TDI, and 2,4-TDI polymerized with butanediol (BD). They were selected to be representative of the chemical structures and morphologies of the hard-segment units in polyurethane elastomers. As in those materials, the 2,4-TDI–BD copolymer is completely amorphous[11] while 2,6-TDI–BD and MDI–BD are capable of crystallizing under the proper conditions.[11,12] It was therefore of interest to examine changes in the spectroscopic properties of the N–H vibration after annealing and determine whether additional information on the nature of hydrogen bonding and chain packing could be obtained from this type of analysis. The temperature dependence of hydrogen

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