meta < ortho; that is to say, the interactions between side chains do not increase the stability of the helical structure. This conclusion is in good agreement with calculations of Finkelstein and Ptitsyn.[16] They determined that among local interactions affecting the helical structure of a polypeptide the interactions of side groups with one another do not play the main role in the stability of the helical form. But these interactions between side chains should play an important role in the α-helix parameters. Clearly, for poly(*p*-nitrobenzyl L-glutamate) the extension in the hydrogen-bond length, and thus in the axial rise per residue, is greatest. The influence of the substitution in the para position of an aromatic ring on the secondary structure is a well-known phenomenon for poly(p-nitrobenzyl L-aspartate).[17] In particular, an anomaly in the axial rise per residue had been shown in this case. Such a variation is more important[18] for poly(*p*-nitrobenzyl L-aspartate) than for poly(*p*-nitrobenzyl L-glutamate) but with the opposite sign. That is to say, the helix of poly(*p*-nitrobenzyl L-aspartate) is more compact than a right-handed α helix, and the helix of poly(*p*-nitrobenzyl L-glutamate) is less compact than a right-handed α helix.

It is difficult to give an explanation of the different side-chain orientations for each poly(nitrobenzyl L-glutamate). It is known that the side-chain orientations can depend on the length of the side chain.[14] But another contribution would be provided by differences, in dipole–dipole interactions. And, of course, the length of the side-chain increases and the dipole–dipole interactions change too when the nitro substituent is moved from the ortho to the para position.

An additional contribution to the greater stability of poly(2,4,6-trimethylbenzyl L-glutamate) and poly(*o*-nitrobenzyl L-glutamate) is perhaps provided by more efficient shielding of the hydrogen-bond helical backbone. Obviously, the 2,4,6-trimethylbenzyl group is bulkier than the benzyl group and the nitro substituent is nearer to the backbone when it is in the ortho position rather in the meta or para position. For both of these polymers the stability of the helical form is greater.

The discrepancy between our results and theoretical calculations[15] for the orientation of side chains, is not surprising since theoretical calculations apply to isolated molecules *in vacuo* whereas our studies are concerned with films. In the solid state, side-chain conformations are probably modified to minimize packing energy.

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(16) A. V. Finkelstein and O. B. Ptitsyn, *J. Mol. Biol.*, **62**, 613 (1971).

(17) M. Goodman, A. M. Felix, C. M. Deber, A. R. Brause, and G. Schwartz, *Biopolymers*, **1**, 371 (1963); M. Hashimoto and J. Aritomi, *Bull. Chem. Soc. Jap.*, **39**, 2707 (1966).

(18) J. B. Aragão and M. H. Loucheux, *J. Chim. Phys.*, 1578 (1971).

Notes

Cleavage of Isotactic Poly(*tert*-butylethylene oxide) by Butyllithium

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The polymerization of *tert*-butylethylene oxide by potassium *tert*-butoxide in bulk has been found[1] to give a crystalline polymer differing in its X-ray diffraction pattern and solution nmr from the crystalline polymer prepared by typical coordination catalysts.[1,2] The latter, presumed to be isotactic, gave the expected erythro dimer glycol on butyllithium degradation.[3] The former gave equal amounts of erythro and threo dimer, supporting the view that the base-catalyzed polymer has a regularly alternating sequence of isotactic and syndiotactic placements.

Since one of the major differences between the poly(*tert*-butylethylene oxide) samples prepared by base and coordination catalysts was the very much higher molecular weight of the latter, we have felt it desirable to degrade the latter to the same molecular weight as the former in order to make a comparison of samples of approximately the same molecular weights.

Experimental Section

Isotactic poly(*t*-BuEO)[2] was prepared by adding 10.5 ml of 16.8 wt % diethylzinc in benzene and 0.23 ml of water to 8 g of *t*-BuEO sealed under N_2 and heated to 60° for 1 week. The crude polymer was extracted several times with benzene, which gave 1.9 g of liquid polymer. After washing with 5% aqueous HCl, the benzene-insoluble polymer was dissolved in 200 ml of tetralin at 90°, filtered, and poured into 1200 ml of methanol: yield 3.1 g, mp 138–143°, $[\eta]$ = 2.14 (90° in tetralin).

"Iso-syn" poly(*t*-BuEO)[1b] was prepared from 3 g of *t*-BuEO and 0.034 g of *t*-BuOK sealed under N_2 and heated to 90° for 21 days. The crude product was dissolved in 150 ml of cyclohexane, neutralized by adding solid CO_2, washed with water thoroughly, dried, and evaporated: yield 3.0 g, mp 52.5–55.5°, $[\eta]$ = 0.057 (30° in benzene), M_n = 4700 (vapor pressure osmometer).

Polymer cleavage of 1 g of isotactic poly(*t*-BuEO) by 0.152 ml of 20.7 wt % butyllithium in hexane (Venturon Corp.) was carried out for 16 hr in 100 ml of refluxing benzene. Then 3 ml of ethanol was added followed by 20 ml of 10% aqueous HCl. After washing to neutrality with water, the insoluble polymer was collected by filtration (0.9 g). Evaporation of the benzene filtrate gave 81 mg of solid polymer: mp 113–120°, $[\eta]$ = 0.139 (30° benzene), M_n = 5000 (vpo). The process was repeated several times with similar results. Cleavage using 1.5 times as much BuLi gave 12–15% degraded polymer, mp 115–117°, $[\eta]$ = 0.101 (30° benzene, M_n = 2800 (vpo)).

The X-ray powder pattern and solution nmr for these degraded isotactic samples were identical with those reported earlier for the undegraded polymer[1b] and quite distinct from those from the base-catalyzed polymer.

Discussion

The experimental results reported here confirm the earlier conclusions that poly(*t*-BuEO) formed by base differs

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(1) (a) C. C. Price and D. Carmelite, *J. Amer. Chem. Soc.*, **88**, 4039 (1966); (b) C. C. Price and H. Fukutani, *J. Polym. Sci., Part A-1*, **6**, 2653 (1968).

(2) G. Allen, C. Booth and S. J. Hurst, *Polymer*, **8**, 385 (1967).

(3) C. C. Price, M. K. Akkapeddi, B. T. DeBona and B. Furie, *J. Amer. Chem. Soc.*, **94**, 3964 (1972).

from that formed by coordination catalysts in the configuration of the asymmetric centers and not merely in molecular weight, since we have now been able to compare directly samples with the two different configurations of essentially the same molecular weight.

Since base-catalyzed polymerization of phenylglycidyl ether has been reported to give crystalline isotactic polymer of low molecular weight,[3] we had hoped to compare this material directly to degraded samples from high molecular weight isotactic polymer formed by coordination catalysts. The recovered degraded polymer proved to be rubbery rather than a crystalline solid. This has to date frustrated this hope. Perhaps one reason for this is the fact that in poly(phenylglycidyl ether) there are both backbone and side-chain ether bonds which may cleave.

Preparation and Properties of a Polymer Formed from Propargyl Azide

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During the investigation of the preparation and properties of new organic azides, it was found that when an alcohol–water solution of propargyl bromide and sodium azide was refluxed, an insoluble polymeric product was formed. It appeared that intermolecular addition had taken place after the propargyl azide was formed by displacement of the bromide, resulting in a polytriazole product. Because of an interest in high nitrogen containing polymers for certain solid rocket propellant applications, the properties of this product, including the heat of combustion, were determined.[1]

Experimental Section

Propargyl Azide; Formation and Polymerization. Solutions of 8.3 g (0.128 mol) of sodium azide in 30 ml of water and 10 ml (0.128 mol) of propargyl bromide in 15 ml of ethanol were mixed in a round-bottom flask; two layers were formed. Heat was evolved upon mixing, and as the displacement reaction proceeded before refluxing an inversion of the layers was observed.

Refluxing of the mixture was initiated and after about 1 hr, the liquid had become one phase and had turned orange; shortly thereafter, a precipitate started to form. After refluxing for about 2 days, 2.7 g (26%) of tan solid was collected and washed with water; a small additional amount of polymer could be precipitated by adding water to the filtrate.[2] The product was dried under vacuum at about 100° before analysis. *Anal.* Calcd for $C_3H_3N_3$: C, 44.45; H, 3.73; N, 51.84. Found: C, 44.04; H, 4.07; N, 49.57; O, 1.97. The oxygen is presumably due to water which had been occluded or chemically bound.

The insolubility of the product in nonreactive organic solvents precluded an exact determination of a molecular weight. It was quite soluble in concentrated sulfuric or hydrochloric acids, and could be reprecipitated by diluting with water. The infrared spectrum and appearance of the reprecipitated product was identical with that of the original material, thus, the solution process in acid did not permanently alter the product. Viscosity measurements were made on an hydrochloric acid solution of the product, from which an intrinsic viscosity was estimated.

Table I
Infrared Data (cm^{-1})

3125 (m)	1325 (m)	1028 (m)
2980 (w)	1220 (s)	975 (w)
1552 (m)	1153 (w)	843 (w)
1450 (m)	1127 (m)	787 (s)
1420 (m)	1050 (s)	

Table II
Energy of Combustion of the Polytriazole

Wt of Sample (g)	Temp Change (°C)	Energy from Fuse Wire (cal)	HNO_3 Formed (mol × 10^4)	$-\Delta E_c$[a] (cal/g)
0.6687	1.476	16.5	1.5	5233
0.4503	1.001	15.5	0.9	5262
0.5610	1.246	17.9	1.1	5260
				Av 5252 ± 12

[a] These values have been corrected for HNO_3 formation; the ΔH_f and ΔH_{sol} for HNO_3 were taken as 42.4 and 7.2 kcal per mol, respectively.[3]

The substance was thermally stable up to 200° but darkened above that temperature; the darkening was accompanied by slow gas evolution, and no sign of melting was observed.

Heat of Combustion. The energies of combustion (ΔE_c) were determined using a Parr, Series 1230, Model 1115, oxygen bomb calorimeter equipped with a Model 2611 adiabatic control system. The standard procedure for a nonvolatile solid was followed. The polymer samples were ground to a fine powder, dried under vacuum, pressed into a soft pellet, weighed, and placed in the bomb. One milliliter of water was placed in the bomb also to saturate the atmosphere with water vapor and to ensure that any HNO_3 formed in the combustion would go into dilute solution. The bomb was evacuated (to the vapor pressure of water), pressurized to 20 atm with oxygen, evacuated again, then repressurized for combustion (30 atm ensured essentially complete combustion).

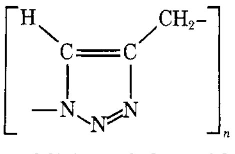
The assembled adiabatic calorimeter was allowed approximately 15 min to equilibrate before temperature readings were taken; temperature readings were taken exactly 4 min before ignition, at ignition, and 9 min after ignition. The uncertainty of the thermometer readings was ±0.0005°.

The calibration of the calorimeter was made with benzoic acid supplied by Parr; the energy of combustion was taken as 6317.8 cal/g. Five samples of benzoic acid were used to determine the energy equivalent of the calorimeter system. The Washburn corrections were applied to the raw data using the methods in Hubbard, Scott, and Waldington.[3] The resulting mean energy equivalent was 2386.9 ± 1.2 cal/deg (±average deviation).

The bomb was carefully rinsed out after combustion of the polymer and the solution titrated with NaOH to determine the HNO_3 content. It was assumed that the HNO_3 was formed exclusively from the nitrogen in the polymer because of the precautions taken to prepare the bomb. This assumption was checked by titrating a solution after combusting a hydrocarbon under similar conditions; no acid was found.

Discussion Section

From the observed properties and composition, the product appears to be primarily a polymer of 4-methylene-1,2,3-triazole



formed by 1,3-cycloaddition of the azido group of one molecule of propargyl azide to the acetylenic bond of another (the 5-methylene configuration is a possibility also and

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(1) The product appears to be similar to that reported by M. C. Baldwin, K. E. Johnson, J. A. Lovinger, and C. O. Parker, *J. Polym. Sci., Part B*, 5, 803 (1967). However, the method of synthesis reported herein is much less hazardous and the polymer has been more fully characterized.

(2) Professor P. A. S. Smith (University of Michigan) has reported to us that if the reaction mixture is stirred for about 1 hr then diluted with water, without having been heated, a liquid product, apparently monomeric propargyl azide is obtained. It distilled near 80°, but exploded with destructive violence before distillation could be completed. The shock sensitivity of propargyl azide has been reported to be greater than that of nitroglycerine.[1]

(3) W. N. Hubbard, D. W. Scott, and C. Waldington in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, Inc., New York, N. Y., 1956, pp 75-104.