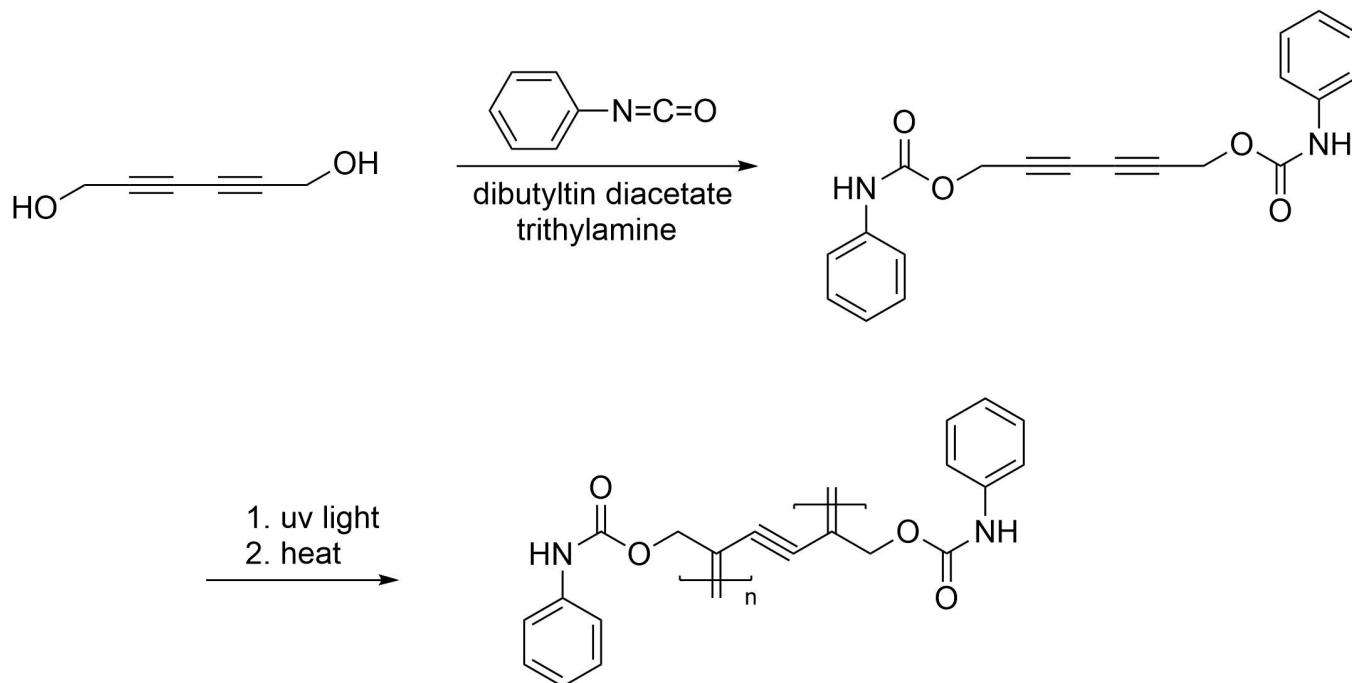


Solid-State Polymerization of 2,4-Hexadiyne-1,6-Diol- bis-(Phenylurethane)

Poly[1,2-bis(Phenylcarbamoyloxymethyl)1-
Buten-3-Ynylene]

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1. Procedure

a. Preparation of 2,4-Hexadiyne-1,6-bis(phenylurethane)

A 250 mL, three-necked flask is fitted with a mechanical stirrer, a condenser protected by a drying tube and a dropping funnel. To the flask are added 5.5 g (0.05 mol) of freshly recrystallized 2,4-hexadiynediol (Note 1) dissolved in 40 mL of anhydrous THF (Note 2) followed by a solution of 0.2 mL of triethylamine and 100 mg of dibutyltin diacetate in 5 mL of anhydrous THF. The flask is immersed in a water bath at 25° and 20 mL of freshly distilled phenylisocyanate is added dropwise over a period of 15 min with rapid stirring. The mixture is then heated to 60° for 3 h. After the mixture is cooled to room temperature, 180 mL of *n*-heptane is added, whereupon the bis(phenylurethane) precipitates as a white, crystalline mass. It is filtered and washed with additional *n*-heptane until freed of residual phenyl isocyanate. The crude bis(phenylurethane) is

recrystallized 3 times from boiling 95% ethanol (Note 3). The yield is 70% after these recrystallizations. Colorless prismatic crystals are obtained having mp 171-172°. The product should be stored in a desiccator in the dark (Note 4).

b. Conversion to the Reactive Monomer

Hexadiyne-1,6-bis(phenylurethane), 1.5 g, freshly recrystallized from ethanol, is dissolved in 150 mL of dioxane (**Caution! Carcinogen**) (Note 5). The solution is filtered into a wide-necked, 500 mL Erlenmeyer flask and warmed to the boiling point of dioxane. Hot water (200 mL) in small portions of about 10 mL is added to the boiling solution with vigorous stirring. The temperature should not drop below 90° during this procedure. As the last portions of hot water are added, the first crystals of the reactive modification of the monomer usually start to separate as fine, colorless needles. The Erlenmeyer flask containing the hot solution is covered with a watchglass and allowed to cool to room temperature over a period of 5 h. The ribbonlike crystals (Note 6) of monomer are then collected on a filter, washed once with 50 mL of a mixture of dioxane and water (1.5, v/v) and dried in a light-protected desiccator over a period of 24 h in vacuo (Note 7). The yield is 86-90%, mp 172° (with decomposition), as determined by differential scanning calorimetry with a heating rate of 8°/min.

c. Polymerization (Note 9)

The crystals, 0.25 g, obtained from the dioxane-water mixture are suspended in a mixture of 5 mL of *n*-propanol and 95 mL of water in a beaker or similar vessel at room temperature (Note 8). The suspension is well stirred with a magnetic stirrer and its surface is irradiated directly with a high pressure mercury lamp (UV-Brenner Q 300, Firma Heraeus, 240 watts). The distance from the lamp to the surface of the suspension is 12 cm. Irradiation is limited to at least 30 sec, but not more than 60 sec. During irradiation the white or faintly blue crystals turn deep blue.

The deep blue crystals are filtered and dried under the conditions described above (Notes 7 and 9). The dried crystals, 0.25 g, are transferred into a test tube that is then sealed with a torch at atmospheric pressure so that the total volume of the glass ampoule is not larger than 15 mL. It is now placed in a thermostat and is kept at exactly 100° for 6 h. **Caution!** The necessary precautions must be taken to ensure that the glass ampoule will be contained if it ruptures while heating. After cooling to room temperature the ampoule is opened and the red-colored crystals of polymer having the original shape of the crystals of monomer are extracted from residual monomer by washing repeatedly with dioxane. The yield is 70-95% after drying in vacuo at room temperature for 24 h.

2. Characterization

The polymer consists of deep-red single crystals with copper-like metallic brilliance. The crystals are triclinic, $a = 4.89$ (fiber axis) $b = 12.53$, $c = 16.77\text{\AA}$; $\alpha = 69.38^\circ$, $\gamma = 96.20^\circ$, $d = 1.37\text{ g/cm}^3$. The space group is $P1$. The asymmetric unit contains one base unit ($\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_4$) and half a molecule of dioxane ($\text{C}_4\text{H}_8\text{O}_2$) in the center of symmetry.³ The all-trans structure of the main-chain of the polymer is a consequence of the solid-state reaction mechanism, being preformed by the packing of the monomer molecules within their lattice.^{3,4,5}

The polymer crystals exhibit strong dichroism with the main axis of absorption parallel to the fiber axis, which was the axis of maximum elongation of the crystals. Independent of the initiator of polymerization (thermal, ultraviolet, x-rays, or γ -rays from Co^{60}), the same polymer is obtained with the same crystallographic data as long as the dioxane adduct does not decompose during polymerization (Note 7). The crystals of the polymer expell dioxane when heated above 150° for

an extended period of time and change into another modification of the polymer. The polymer decomposes readily at temperatures above 250° and does not show a melting point. The polymer dissolves in hexamethylphosphoric acid triamide (**Caution! Carcinogen**) containing 5% lithium chloride and 0.5% phthalic acid anhydride at temperatures between 50 and 60°. No other solvent is known. The solutions are a deep red to orange color. Values of η_{sp}/c as high as 20 dL/g are obtained in this solvent, as measured with an Ostwald viscometer at 30° ($c = 0.1$ g/dL). The polymer in solution decomposes readily, especially in the presence of traces of amines at temperatures above 60°. The UV spectra of the polymer crystals show a rather broad absorption maximum at 490 nm.

3. Notes

1. 2,4-Hexadiynediol is prepared according to the method of Reepe and coworkers⁴ by oxidative dimerization of propargyl alcohol, and is recrystallized from ethyl acetate, mp 112°. It should be stored in a light-protected desiccator, because the crystalline dialcohol forms an insoluble polymer in diffuse daylight.⁵ 2,4-Hexadiynediol is also commercially available from Chemical Samples Co., 4692 Kenny Road, Columbus, Ohio 43220. If the experimenter wishes to prepare his own diol, the following procedure may be used: A solution of 24 g of propargyl alcohol dissolved in 40 mL of ethanol is dropped over a period of 20 min into a mixture of 160 g of ammonium chloride, 120 g of copper chloride, 1.8 mL of conc. HCL, and 500 mL of water contained in a 2 L, three-necked flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser. During addition of the propargyl alcohol, the flask is cooled with a water bath so that the temperature of the reaction mixture does not rise above 35°. The dropping funnel is then replaced with a gas-inlet tube and a stream of oxygen is bubbled through the mixture at a rate of 2.5 L/h with vigorous stirring and without further cooling. After ca 2 h, the initially brown to yellow color of the mixture changes to light green. The reaction mixture is now saturated with sodium chloride, and the insoluble salts are filtered. The filtrate is extracted 4 times with 250 mL of ethyl acetate. The combined extracts are dried over sodium sulfate and ethyl acetate, then distilled under reduced pressure. Brownish crystals of 2,4-hexadiynediol, 18 g, are obtained as the residue.

2. THF is refluxed over sodium wire and distilled immediately before use.

3. About 100 mL of 95% ethanol is used to recrystallize 5 g of the monomer. It is strongly recommended that the monomer be recrystallized at least 3 times from boiling ethanol to eliminate the last traces of phenyl urea, which is formed as a by-product during the monomer synthesis in the presence of water. Phenyl urea inhibits the thermal polymerization.

4. The modification obtained by crystallization from ethanol is slightly light sensitive. The checker found a melting point of 167 - 168° rather than the 171 - 172° reported by the submitters using differential scanning calorimetry.

5. Commercial grade dioxane may be used.

6. To obtain large crystals for use for physical measurements, slow cooling is needed. The authors successfully prepared long, ribbon-like crystals several centimeters in length by putting the hot solution in test tubes of 2 cm diameter in a thermostat at 96°. The temperature of the thermostat was then lowered at a rate of 5°/day until a temperature of 60° was reached. This temperature was kept constant until crystallization was completed, after 10-15 days.

7. The modification obtained from dioxane-water is very light sensitive and usually turns blue even during the crystallization and drying process. However, conversion to polymer is less than 1% if the compound is not handled in a clean desiccator (no nitrogen bleed) over pellets of potassium hydroxide or a similar drying agent. In the presence of vapors of organic solvents such as ethyl acetate, THF, or acetonitrile the reactive modification, which is an adduct of dioxane with the bisphenylurethane³, is converted from reactive to inactive. If contamination of the crystals with these solvents is avoided, no problems from overdrying and loss of dioxane are encountered.

8. Freshly prepared crystals that have not yet been dried may also be used.

9. It was found that to obtain soluble polymer in a reproducible way, polymerization is best carried out in two steps. The first step consists of photopolymerization to less than 5% conversion. The second step is thermal polymerization in the dark at elevated temperature to obtain high conversion. In principle, thermal polymerization alone would suffice. However, sometimes complications arise because of the change in crystal modification from reactive to nonreactive which takes place at polymerization temperature. The change in modification occurs unreproducibly and seems to depend on the method of crystallization and purification of the monomer crystals. Whenever the change in modification occurs, insoluble polymer is obtained. Photopolymerization prior to thermal polymerization stabilizes the metastable reactive dioxane adduct of the monomer. Further information on modifications of 2,4-hexadiynediol-bis(phenyl urethane) and solid-state reactivity has been published.⁶ Photopolymerization alone would also be insufficient, because the polymer absorbs short wavelength radiation, thereby protecting the monomer inside the crystals from further photopolymerization. The dependence of photopolymerization on wavelength⁷ and the dependence of thermal polymerization on temperature⁴ have been noted. Polymerization temperature normally should not exceed 110° and may be as low as 80°. Reaction time has to be increased accordingly at lower temperatures and decreased at higher temperatures to obtain maximum conversion and soluble polymers.

4. References

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