bands; the olefin bands at 1799 and 892 ($RR'C{=}CH_2$) and 1630 cm^{-1} ($C_3H_5C{=}C$) had disappeared. The average molecular weight of the product, determined by vapor pressure osmometry, was 1219. This corresponded to a little more than six units of monomer (molecular weight of α-heptylstyrene is 202).

F. Polymerization of α-Nonylstyrene. This compound was polymerized in a manner identical with that of α-heptylstyrene, the initiation and reaction times being the same. In this case, however, 8.5 g of monomer dissolved in 50 ml of tetrahydrofuran was used. The infrared spectrum was very similar to that of the polymerized α-heptylstyrene. All the olefin bands were missing. The average molecular weight, determined by vapor pressure osmometry, was 1202 which corresponds to 5.2 units of monomer (molecular weight of α-nonylstyrene is 230).

1,3-Dipolar Addition Polymerizations. The Synthesis and 1,3-Dipolar Addition Polymerization of Dipole–Dipolarophile (A–B) Monomers Containing Tetrazole and Vinyl or Ethynyl Moieties

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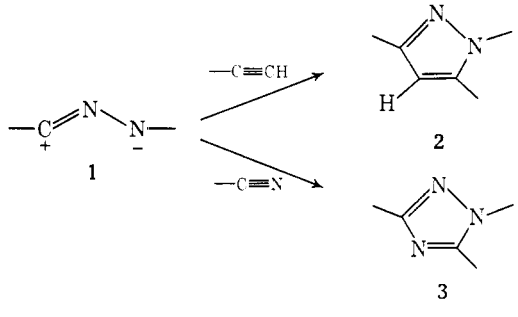
ABSTRACT: The syntheses of two new A–B monomers containing a tetrazole moiety connected by a *p*-phenylene bridge to a vinyl or ethynyl group has been carried out. The 1,3-dipolar homopolymerization of the two A–B monomers yielded poly(1-phenyl-3-*p*-phenylene-Δ^2-pyrazoline) (**11**) and poly(1-phenyl-3-*p*-phenylenepyrazole) (**12**). The polymers possessed intrinsic viscosities of 0.58 and 0.75 and were stable in air to 360 and 460°, respectively. The polymers were soluble in polar and acidic solvents.

A number of 1,3-dipolar cycloaddition reactions have been employed for the formation of five-membered heterocycles; the mechanistic and kinetic aspects of many of these reactions are now reasonably well established.[2] The products of the 1,3-dipolar cycloaddition of nitrilimines (**1**) to acetylenes and nitriles are pyrazoles (**2**) and triazoles (**3**). The 1,3-dipolar cycloaddition reaction of nitrilimines is a useful polymer-forming reaction since the reactions often proceed in high yield, and the product linkages (**2, 3**) contain an aromatic sextet desirable for good thermal stability. Suitable nitrilimine dipoles may be generated either by treating hydrazide chlorides, in solution, with a base such as triethylamine, or by the pyrolysis of 2,5-disubstituted tetrazoles.[2] Polymerization studies carried out in this laboratory with bishydrazide chlorides and bistetrazoles have shown the tetrazole ring to be a superior nitrilimine precursor with respect to polymer yield and molecular weight.[3–5] A polypyrazole having an intrinsic viscosity of 1.67 (0.300 g/100 ml of 98% formic acid at 30°) and a thermal stability in air to nearly 500° has been obtained[5] from the reaction of a bistetrazole with a diethynyl compound. Although thermally stable polymers of moderate molecular weight could be synthesized using bistetrazoles as nitrilimine precursors, the syntheses of A–B monomers containing both the dipole and the dipolarophile were desirable.



Discussion

Monomer Syntheses. In choosing a synthetic pathway for 2-phenyl-5-(4′-vinyl)phenyltetrazole (**4**) and 2-phenyl-5-(4′-ethynyl)phenyltetrazole (**5**) (Scheme I), consideration was given to the relative reactivities of the functional groups present (tetrazole and vinyl or ethynyl) in the two A–B monomers. The tetrazole ring was synthesized first for several reasons: first, the aldehyde precursor of the tetrazole ring is unstable to the conditions required to generate a vinyl or ethynyl group, and second, the vinyl and ethynyl groups could be expected to decompose partially during the synthesis of the tetrazole if they were already present in the system. In addition, the tetrazole ring is relatively stable to the reagents required for the synthesis of the vinyl or ethynyl groups. Reaction of the phenylhydrazone of *p*-tolualdehyde (**6**), with phenyl azide in 2-methoxyethanol containing sodium 2-methoxyethoxide, afforded 2-phenyl-5-(4′-methyl)phenyltetrazole (**7**) in

(1) Lubrizol Fellow, 1968–1969.

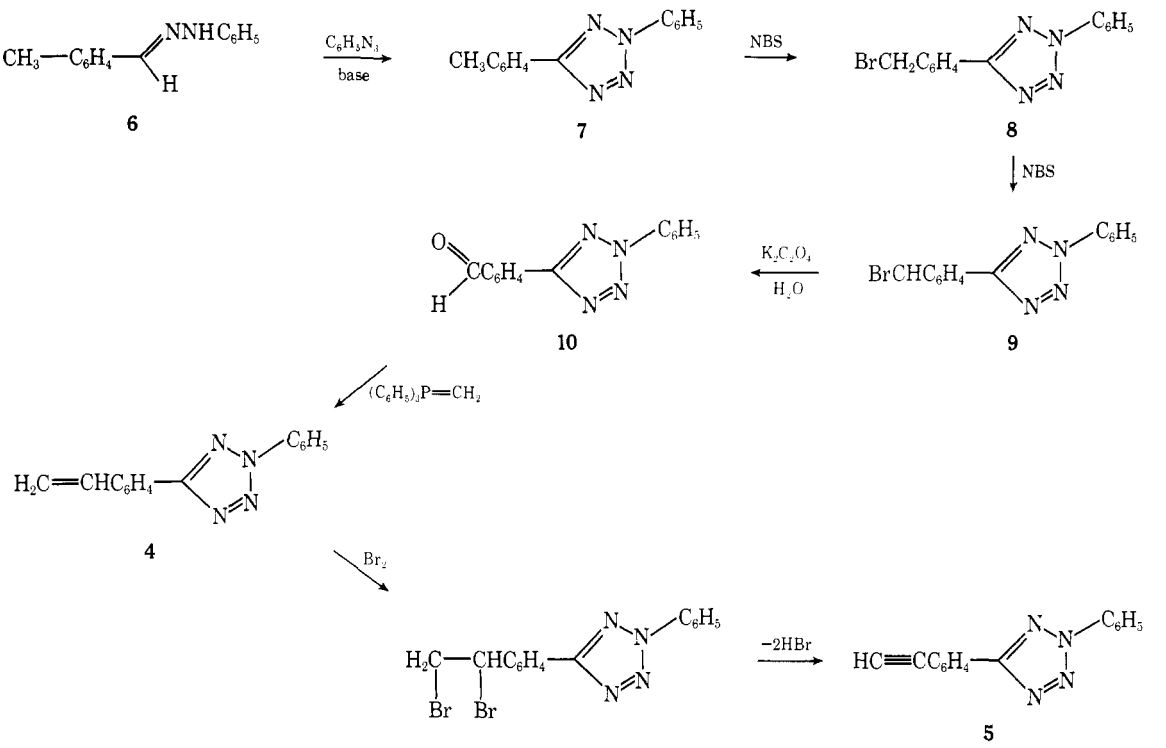
(2) (a) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); *Chem. Weekbl.* (Amsterdam), **59**, 89 (1963); Dechema Monograph., **49**, 201 (1964); *Bull. Soc. Chim. Fr.*, 3431 (1965); (b) R. A. Firestone, *J. Org. Chem.*, **33**, 2285 (1968); (c) R. Huisgen, *ibid.*, **33**, 2291 (1968).

(3) J. K. Stille and F. W. Harris, *J. Polym. Sci., Part B*, **4**, 333 (1966).

(4) J. K. Stille and F. W. Harris, *ibid., Part A*, **6**, 2317 (1968).

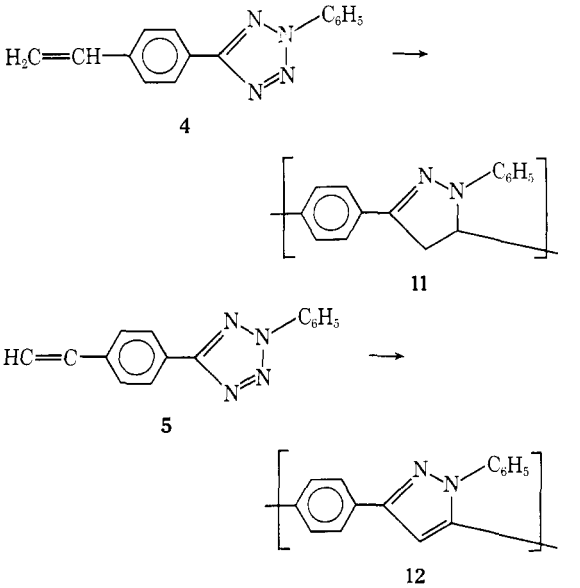
(5) J. K. Stille and L. D. Gotter, *ibid., Part B*, **6**, 11 (1968).

SCHEME I



a 57% yield. The highest yield was obtained when the reaction was carried out over a 10-hr period. Heating the reaction mixture for longer periods resulted in a greatly reduced yield of product and a large amount of intractable material. It was necessary to add the phenyl azide dropwise to a hot solution (110°) of the phenylhydrazone and base over a period of 4–6 hr to obtain the best yield. Also, this prevented a dangerous buildup of phenyl azide which is sensitive to heat. The free-radical bromination of **7** by N-bromosuccinimide in carbon tetrachloride provided 2-phenyl-5-(4′-bromomethyl)phenyltetrazole (**8**) in 57% yield. The progress of the reaction was followed by observing the amount of succinimide appearing at the surface of the reaction mixture and the amount of unreacted N-bromosuccinimide remaining at the bottom of the flask. The reaction appeared to be complete in 8 hr but 21% of the starting material was recovered from the reaction mixture. On the basis of reacted material, the yield was 73%. The free-radical bromination of **8** under conditions similar to those used for **7** yielded 2-phenyl-5-(4′-dibromomethyl)phenyltetrazole (**9**) in 74% yield. In this case, approximately 5% of the starting material was recovered. Hydrolysis of the dibromide **9** in 70% aqueous ethanol containing potassium oxalate gave 4-[5′-(2′-phenyltetrazoyl)]benzaldehyde (**10**). The use of alcoholic recrystallization solvents containing less than 10% water tended to promote the formation of the aldehyde hemiacetal which was undesirable. Treatment of the aldehyde **10** with the Wittig reagent, triphenylphosphorus methylene, afforded a 50% yield of 2-phenyl-5-(4′-vinyl)phenyltetrazole (**4**). The addition of bromine to the double bond of **4** followed by dehydrobromination with potassium *t*-butoxide provided 2-phenyl-5-(4′-ethynyl)phenyltetrazole (**5**). Since the dibromo adduct of **4** decomposed slowly at room temperature, it was not isolated in pure form.

Cycloaddition Polymerizations. The 1,3-dipolar homopolymerizations of 2-phenyl-5-(4′-vinyl)phenyltetrazole (**4**) and 2-phenyl-5-(4′-ethynyl)phenyltetrazole (**5**) were carried out in evacuated sealed reaction tubes in the presence of solvents such as dimethylformamide, hexamethylphosphoramide, and 1,2,4-trichlorobenzene. The light brown polymers, polypyrazoline **11**, and polypyrazole **12** were obtained in 86 and 89% yields, respectively. The polymers were soluble in hexamethylphosphoramide, dimethylformamide, formic acid and sulfuric acid, but not in benzene, chlorobenzene, or 1,2,4-trichlorobenzene. When 1,2,4-trichloroben-



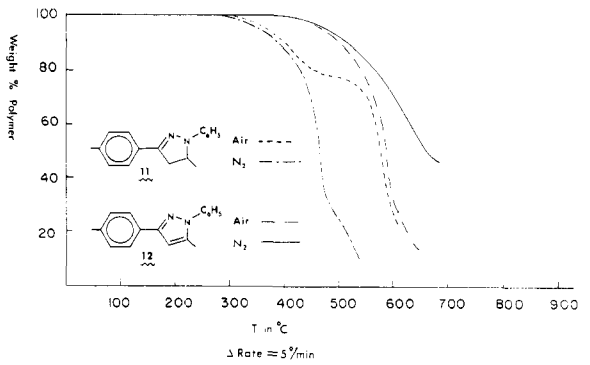


Figure 1. Thermogravimetric analyses of polypyrazoline 11 and polypyrazole 12.

zene was used as the polymerization solvent, polymers **11** and **12** were insoluble gels. Polymers **11** and **12** were stable in air to 360 and 460°, respectively (Figure 1), and possessed intrinsic viscosities of 0.58 and 0.75 (0.300 g/100 ml of dimethylformamide at 30°).

Experimental Section

***p*-Tolualdehyde Phenylhydrazone (6).** The reaction of *p*-tolualdehyde with phenylhydrazine was carried out according to the known procedure[6,7] to afford the phenylhydrazone, mp 114–114.5° (lit.[7] mp 114°).

2-Phenyl-5-(4′-methyl)phenyltetrazole (7). This compound was prepared as described[6] by the reaction of *p*-tolualdehyde phenylhydrazone with phenyl azide in basic solution, mp 93.5–95° (lit.[6] mp 92–93°).

2-Phenyl-5-(4′-bromomethyl)phenyltetrazole (8). A solution of 32.8 g (141 mmol) of 2-phenyl-5-(4′-methyl)phenyltetrazole and 21.1 g (123 mmol) of N-bromosuccinimide in 300 ml of dry carbon tetrachloride was heated at the reflux temperature for 8 hr. After the mixture had started to reflux, 0.10 g of benzoyl peroxide was added as a free-radical initiator. The mixture was filtered while still hot to remove the insoluble succinimide formed in the reaction. Cooling of the filtrate resulted in crystallization of the 2-phenyl-5-(4′-bromomethyl)phenyltetrazole. Filtration of the solution followed by recrystallization of the precipitate from carbon tetrachloride afforded 25.2 g (57.4%) of white crystals, mp 135–137°.

Anal. Calcd for $C_{14}H_{11}N_4Br$: C, 53.37; H, 3.49; N, 17.77. Found: C, 53.56; H, 3.38; N, 17.54.

2-Phenyl-5-(4′-dibromomethyl)phenyltetrazole (9). A mixture of 25.0 g (8.00 mmol) of 2-phenyl-5-(4′-bromomethyl)-phenyltetrazole and 14.0 g (8.00 mmol) of N-bromosuccinimide in 250 ml of dry carbon tetrachloride was heated to the reflux temperature and 0.10 g of benzoyl peroxide was added as a free-radical initiator. The mixture was heated at the reflux temperature for 6 hr, then the succinimide was removed from the hot solution by filtration. The solution was allowed to cool and the light yellow precipitate which formed was filtered and then recrystallized from carbon tetrachloride to give 23.1 g (74.3%) of white crystals, mp 137–138°.

Anal. Calcd for $C_{14}H_{10}N_4Br_2$: C, 42.64; H, 2.54; N, 14.21. Found: C, 42.47; H, 2.38; N, 13.73.

4-[5′-(2′-Phenyltetrazoyl)]benzaldehyde (10). A solution of 15.6 g (4.00 mmol) of 2-phenyl-5-(4′-dibromomethyl)-phenyltetrazole and 14.0 g of potassium oxalate in 300 ml of 70% ethanol was heated at the reflux temperature for 70 hr. The solution was then allowed to cool, 5.0 g of disodium phosphate heptahydrate was added, and the solution was stirred for 1 hour. The mixture was filtered and the precipitate was discarded. The filtrate was allowed to evaporate to dryness and the solid residue was recrystallized once from benzene and twice from 90% methanol to give 8.5 g (85.0%) of white crystals, mp 127–128°.

Anal. Calcd for $C_{14}H_{10}N_4O$: C, 67.20; H, 3.99; N, 22.38. Found: C, 66.91; H, 3.87; N, 22.16.

2-Phenyl-5-(4′-vinyl)phenyltetrazole (4). To 1000 ml of liquid ammonia, in an atmosphere of dry nitrogen, was added a small amount of anhydrous ferric chloride and 8.30 g (360 mmol) of sodium in small portions. The solution was allowed to stand for 1 hr, then 112 g (342 mmol) of triphenylmethylphosphonium bromide[8] was added with stirring. The ammonia was allowed to evaporate and 1000 ml of ether which had been freshly distilled from lithium aluminum hydride was added. A solution of 60.0 g (231 mmol) of aldehyde **10**, mp 135–137°, in 1000 ml of benzene was heated to the reflux temperature of the benzene and was then added to the refluxing ether solution of triphenylphosphorus methylene over a period of 15 min. The solution was stirred for 15 min, then filtered, and the solvents were removed under reduced pressure. The light yellow residue was divided into three portions. Each portion was placed on a column of 200 g of chromatographic grade alumina (Merck) which had been packed from a slurry in Skellysolve C. The column was eluted with 2 l. of Skellysolve C. The first eight fractions (approximately 200 ml each) from each column were evaporated to dryness under reduced pressure to give 23.6 g (48.0%) of **4**, mp 70–71°. The material was recrystallized once from Skellysolve C and washed with cold Skellysolve C to give an analytical sample, mp 70.5–71.0°.

Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.89; H, 4.75; N, 22.21.

2-Phenyl-5-(4′-ethynyl)phenyltetrazole (5). A solution of 5.00 g (20.0 mmol) of 2-phenyl-5-(4′-vinyl)phenyltetrazole in 100 ml of carbon tetrachloride was cooled to 0°. A solution containing 15% by weight of bromine in carbon tetrachloride was added dropwise until the solution of **4** retained the red bromine color for 2 min after the previous drop of bromine solution had been added. Evaporation of the solvent under reduced pressure and recrystallization from Skellysolve C at low temperature afforded cream colored crystals which started to turn brown in air at room temperature. The product was stored at Dry Ice temperature until use. The crystalline intermediate was added to a solution of 75 ml of *t*-butyl alcohol in which 1 g-atom of potassium metal was dissolved. The solution was stirred and heated at the reflux temperature for 1 hr and then poured over 300 g of crushed ice. The mixture was filtered, the white precipitate was dried under reduced pressure, dissolved in benzene, and chromatographed on a 50-cm column of alumina with benzene as the eluent. Three 50-ml fractions were collected and evaporation of the solvent from the first two fractions afforded 2.90 g (59.2%) of white crystals, mp 92–93.5°.

Anal. Calcd for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75. Found: C, 73.34; H, 4.10; N, 22.57.

Poly(1-phenyl-3-*p*-phenylene-Δ^2-pyrazoline) (11). A solution of 0.500 g (2.00 mmol) of 2-phenyl-5-(4′-vinyl)phenyltetrazole in 5 ml of dimethylformamide was sealed in a glass polymerization tube under reduced pressure in the absence of oxygen by subjecting the mixture to several

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(7) S. Y. Hong and J. E. Baldwin, *Tetrahedron*, **24**, 3787 (1968).

(8) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 1954).

freeze–evacuate–thaw cycles at liquid nitrogen temperature. The tube was placed in a Parr bomb (which also contained dimethylformamide to equalize internal and external pressures) and heated at 150° for 4 hr. The tube was then opened and the solution was poured into rapidly stirred methanol. The precipitated material was filtered and then dried *in vacuo* at 212° for 12 hr to afford 0.379 g (86.1%) of yellowish brown polymer, η = 0.58 (0.300 g/100 ml of dimethylformamide at 30°).

Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.82; H, 5.48; N, 12.73. Found: C, 81.31; H, 5.83; N, 12.58.

Poly(1-phenyl-3-*p*-phenylenepyrazole) (12). The polymerization of 2-phenyl-5-(4′-ethynyl)phenyltetrazole was carried out as described for 2-phenyl-5-(4′-vinyl)phenyltetrazole to provide 0.387 g (88.6%) of light brown polymer, η = 0.75 (0.300 g/100 ml of dimethylformamide at 30°).

Anal. Calcd for $C_{15}H_{10}N_2$: C, 82.56; H, 4.58; N, 12.84. Found: C, 82.67; H, 4.70; N, 12.03.

Free-Radical Polymerization of 2-Phenyl-5-(4′-vinyl)phenyltetrazole. Reactivity Ratios and Q and e Values

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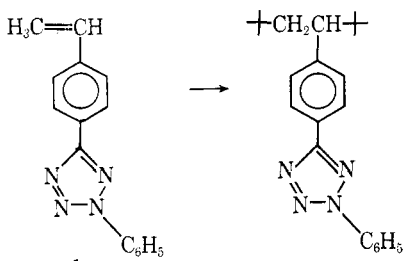
ABSTRACT: The monomer, 2-phenyl-5-(4′-vinyl)phenyltetrazole (**1**), has been homopolymerized and copolymerized with styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile by free-radical initiation. Elemental analyses data have been used to calculate reactivity ratios and Q and e values for the tetrazoylstyrene monomer. Thermal cross-linking of the tetrazoylstyrene–acrylonitrile copolymer has been accomplished by the 1,3-dipolar cycloaddition reaction of the nitrilimine dipole across the nitrile dipolarophile. The tetrazoylstyrene monomer is similar to styrene in terms of reactivity in copolymerization (Q = 0.75, e = 0.6).

In many polymer systems, a controlled degree of cross-linking subsequent to the polymer forming reaction is desirable, particularly when the cross-linking renders the polymer insoluble and provides memory with respect to dimensional stability without providing brittleness. A monomer which can serve as a potential cross-linking agent in vinyl polymerization systems is of particular significance when selective and controlled cross-linking can be accomplished in one of the final steps in the conversion of polymer to product. The monomer, 2-phenyl-5-(4′-vinyl)phenyltetrazole (**1**) synthesized for use in 1,3-dipolar cycloaddition polymerizations,[2] has the potential of undergoing vinyl addition copolymerization and subsequently reacting with suitable dipolarophiles in the polymer chain formed to afford a cross-linked polymer by thermal treatment. The purpose of this investigation was to homopolymerize **1** and to copolymerize it with a series of vinyl monomers including one containing a dipolarophile which would be present after the free-radical polymerization had occurred.

Discussion

The free-radical homopolymerization reactions of **1** in a benzene solvent with azodiisobutyronitrile as an initiator provided poly{4-[5′-(2′-phenyltetrazoyl)]-styrene} (**2**) in 68% yield. The polymer was very similar to styrene in solubility and color and possessed an intrinsic viscosity of 0.80 (0.300 g/100 ml of dimethylformamide at 30°). Since monomer **1** could be expected to have copolymerization characteristics similar to styrene, a series of four vinyl monomers—styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile—were selected for copolymerization. The copolymerization reactions were carried out in a benzene solvent within evacuated, sealed polymerization tubes at 60°. The polymerization reactions were stopped at less than 10% conversion and, as a result, the polymerization time varied from 1 to 4 hr, depending on the reactivity of the comonomers. By stopping the reaction at less than 10% conversion, a major change in monomer concentration from the initial charge did not occur and the general method for the solution of the copolymer equation could be used.



1 2

The polymerization of 2-phenyl-5-(4′-vinyl)phenyltetrazole (**1**) with the comonomers styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile produced the copolymers **3, 4, 5,** and **6** containing both the monomer **1** and the respective comonomers in the polymer chains (Scheme I). The polymers were isolated by precipitation into methanol, purified by reprecipitation, and dried by lyophilization from benzene. Duplicate analyses for carbon and nitrogen were

(1) Lubrizol Fellow, 1968–1969.
(2) J. K. Stille and L. D. Gotter, *Macromolecules*, 2, 464 (1969).