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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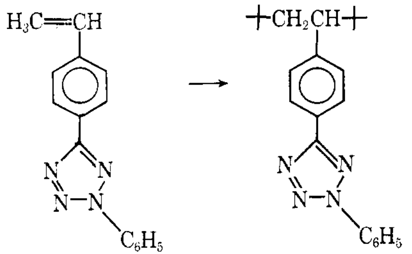
ABSTRACT: The monomer, 2-phenyl-5-(4′-vinyl)phenyltetrazole (1), has been homopolymerized and copolymerized with styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile by free-radical initiation. Elemental analyses data have been used to calculate reactivity ratios and *Q* and *e* values 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

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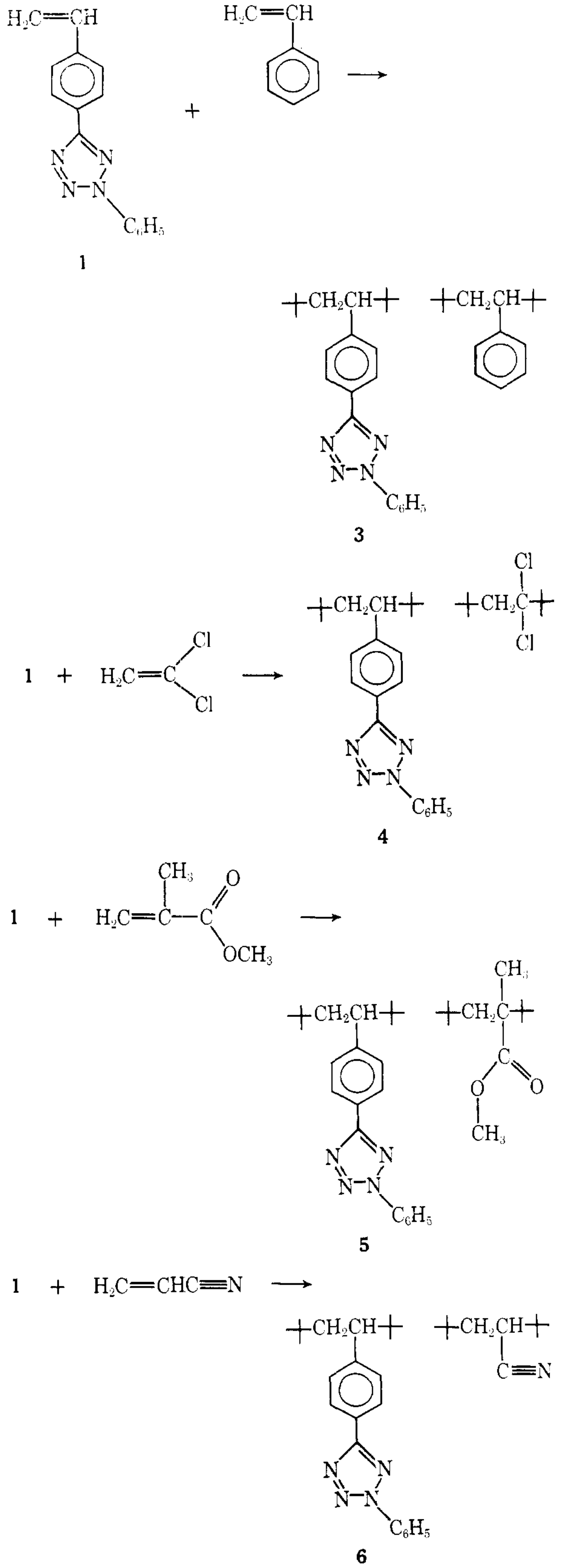
[1] Lubrizol Fellow, 1968–1969.

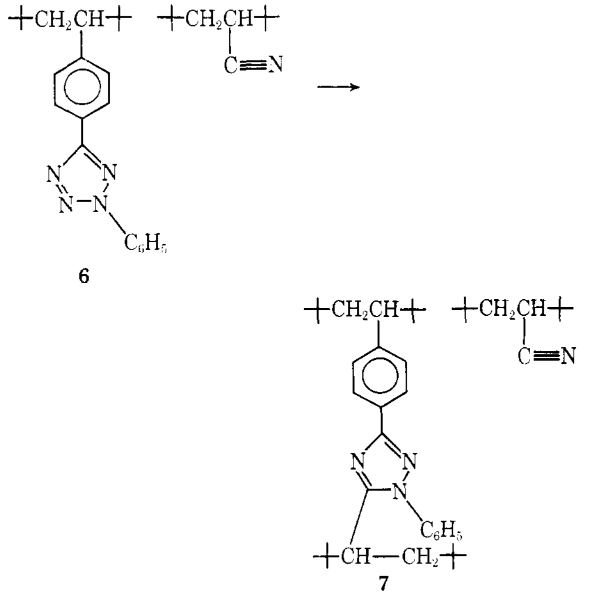
[2] J. K. Stille and L. D. Gotter, *Macromolecules*, 2, 464 (1969).

SCHEME I



carried out on copolymers **3**, **4**, **5**, and **6**. It was possible therefore to calculate the relative amount of each monomer present in a polymer using either the carbon or nitrogen analysis data.

Samples of polymer **6** were heated in solution to above the decomposition temperature of the tetrazole ring to effect cross-linking of the polymer chains by the reaction of nitrilimine and nitrile moieties. A light yellow polymer was obtained which was insoluble in sulfuric acid, formic acid, dimethylformamide, and common organic solvents such as benzene, toluene, chlorobenzene, and 1,2,4-trichlorobenzene. The polymer was assumed to be partially cross-linked as a result of the formation of the triazole linkage **7** through the reaction of the tetrazole dipole with the pendant nitrile dipolarophiles. Although acrylonitrile copolymers can be cross-linked by heating in DMF at 140°,[3] acrylonitrile–styrene copolymers containing 30 mol % styrene afford only 12% insoluble polymer after 1 hr. Copolymer **6**, which contained the same mole per cent tetrazoylstyrene, precipitated immediately on heating to give 98% insoluble polymer. The copolymers, with the exception of the cross-linked polymer **7**, were white and soluble in benzene. Copolymer **6** consistently gave elemental nitrogen analyses values below those theoretically possible for any monomer combination in the copolymer. An attempt was made to decompose thermally the tetrazole rings present in copolymer **6** in a vacuum system and by pressure changes measure the evolved nitrogen so that the composition of the polymer could be determined. Because of the nature of the decomposition (rapid and exothermic), and because nitrogen was not the only volatile decomposition product produced at the decomposition temperature (200°) in the vacuum system, no suitable polymer composition data was obtained. The calculation of reactivity ratios for copolymer **6** was not carried out. The reason for the incorrect analyses is unknown; since nitriles function as dipolarophiles in the presence of the nitrilimine dipole, however, it is possible that upon heating during the analysis, thermally stable cross-links may form which are difficult to oxidize.



The analyses data obtained from the copolymers have been used to calculate the reactivity ratios for the different monomer pairs by both the intersection

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(3) N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).

TABLE I
REACTIVITY RATIO OF 2-PHENYL-5-(4′-VINYL)PHENYLTETRAZOLE (1) WITH COMONOMERS

Method of calcn, eq	Based on carbon analyses r_1	Based on carbon analyses r_2	Based on nitrogen analyses r_1	Based on nitrogen analyses r_2
		Styrene Comonomer		
1	1.26 ± 0.01	0.89 ± 0.06	0.67 ± 0.01	0.98 ± 0.02
2	1.40 ± 0.01	1.00 ± 0.06	0.59 ± 0.01	0.92 ± 0.02
3	1.30 ± 0.01	0.90 ± 0.06	0.66 ± 0.01	0.95 ± 0.02
		Vinylidene Chloride Comonomer		
1	2.24 ± 0.25	0.24 ± 0.02	1.49 ± 0.15	0.26 ± 0.03
2	1.89 ± 0.25	0.22 ± 0.02	1.19 ± 0.15	0.25 ± 0.03
3	2.54 ± 0.25	0.25 ± 0.02	1.64 ± 0.15	0.29 ± 0.03
		Methyl Methacrylate Comonomer		
1	0.22 ± 0.10	0.73 ± 0.03	0.55 ± 0.12	0.86 ± 0.20
2	0.16 ± 0.10	0.44 ± 0.03	0.45 ± 0.12	0.82 ± 0.20
3	0.26 ± 0.10	0.50 ± 0.03	0.68 ± 0.12	0.86 ± 0.20

TABLE II
Q AND *e* VALUES FOR
2-PHENYL-5-(4′-VINYL)PHENYLTETRAZOLE (1)

Comonomer	*Q*	*e*
Styrene	0.9	−0.6
Vinylidene chloride	0.65	−0.5
Methyl methacrylate	0.7	−0.7

method[4] (eq 1) and by direct use of the copolymer equation. Equation 1 is a rearranged form of the integrated copolymerization equation. The terms M_1^0 and M_2^0 are the initial monomer concentrations while M_1 and M_2 are the concentrations of monomers remaining after polymerization has been halted.

$$\mu = \frac{\log \dfrac{M_2^0}{M_2} - \dfrac{1}{\rho} \log \dfrac{1 - \rho \dfrac{M_2}{M_1}}{1 - \rho \dfrac{M_2^0}{M_1^0}}}{\log \dfrac{M_1^0}{M_1} + \log \dfrac{1 - \rho \dfrac{M_2}{M_1}}{1 - \rho \dfrac{M_2^0}{M_1^0}}} \qquad (1)$$

$$\rho = \frac{1 - \sigma}{1 - \mu}$$

Arbitrary values of ρ were used in the equation to obtain a series of μ, σ coordinates for each sample. The coordinates for each sample were graphed and a line was constructed through each set of points representing a copolymer composition. The r_1 and r_2 values listed in Table I, calculated by the intersection method, are the arithmetic mean of the valid intersections shown in the figures following it. The error of this method was determined by dividing the difference between the maximum and minimum values of the intersection by two. The second general method involves the use of the copolymerization equation directly.[5] Equations 2 and 3 are two forms of the copolymerization equation in which f is the ratio of monomer M_1 to monomer M_2 initially, and $F = m_1/m_2$ where m_1 and m_2 are the concentrations of the monomer units incorporated into the polymer.

$$\frac{F}{f}(f - 1) = r_1\frac{F^2}{f} - r_2 \qquad (2)$$

$$\frac{f - 1}{F} = -r_2\frac{f}{F^2} + r_1 \qquad (3)$$

A plot of $F/f(f - 1)$ as ordinate and F^2/f as abcissa (eq 2) gave a line whose slope was r_1 and whose intercept was $-r_2$. A plot of $(f - 1)/F$ as ordinate and f/F^2 as abcissa (eq 3) yields a line whose intercept is r_1 and whose slope is $-r_2$. The r_1 and r_2 values calculated by this method were determined from plots constructed after a least-square analysis of the experimental data was performed. The r_1 values calculated for the different copolymers, from carbon and nitrogen analyses data, by the various methods, show a fairly wide variation while the r_2 values for these same copolymers are in close agreement. The r_2 values for styrene, vinylidene chloride, and methyl methacrylate fell in the range of 0.89–1.00, 0.22–0.29, and 0.44–0.86, respectively. Only two r_2 values for methyl methacrylate were below 0.7. The r_1 values obtained with the comonomers styrene, vinylidene chloride, and methyl methacrylate ranged from 0.65 to 1.35, 1.19 to 2.54, and 0.21 to 0.55, respectively. The selection of a set of r_2 values of 0.95 (styrene), 0.25 (vinylidene chloride), and 0.7 (methyl methacrylate) for determining Q and e (Table II) for 2-phenyl-5-(4′-vinyl)phenyltetrazole was apparent but the selection of a set of r_1 values was more arbitrary. The greatest discrepancy in the r_1 values appeared to be with the method of analysis (carbon or nitrogen), so that the r_1 value selected was an approximate average of the high and low sets, 1.0 (styrene), 1.8 (vinylidene chloride), and 0.4 (methyl methacrylate).

Since **1** is electronically and structurally similar to styrene, a set of Q and e values similar to those of styrene (Q = 1.0, e = −0.8) would be expected.[6] The e values determined for **1** from data obtained with the three comonomers agree quite well; however, there is a somewhat greater variation in Q. The results (Q = 0.75, e = −0.6) show that 2-phenyl-5-(4′-vinyl)-phenyltetrazole (**1**) is similar to styrene in free-radical copolymerization reactions. The slightly less negative

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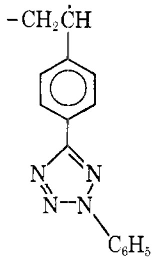
(4) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).

(5) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

(6) T. Alfrey, Jr., and C. C. Price, *ibid.*, **2**, 10 (1947).



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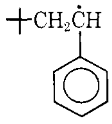

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e value for **1** indicates that the tetrazole ring is electron withdrawing, thus making the tetrazoylstyrene radical **8** less electron rich than the styryl radical **9**.

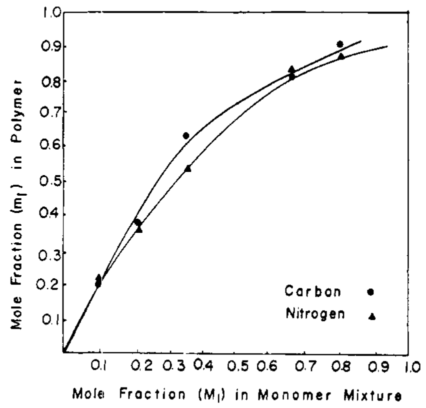

Figure 1. Copolymer composition curve for the polymerization with styrene.

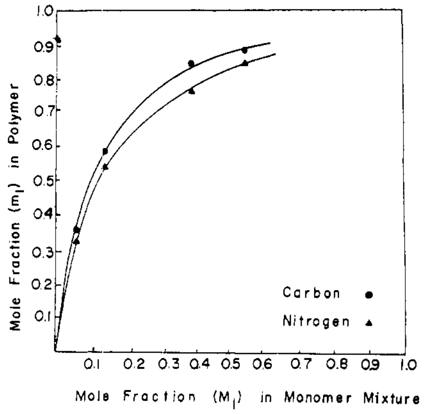

Figure 2. Copolymer composition curve for the polymerization with vinylidene chloride.

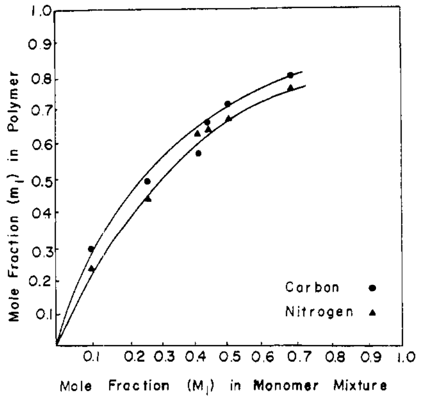

Figure 3. Copolymer composition curve for the polymerization with methyl methacrylate.

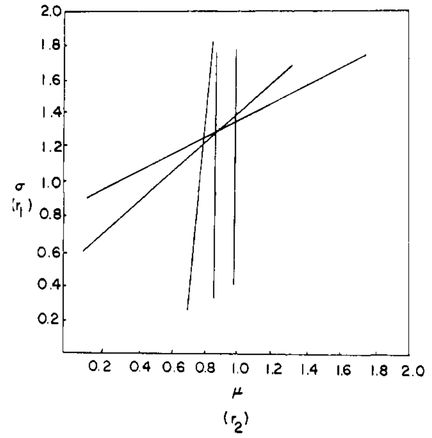

Figure 4. Reactivity ratio for 2-phenyl-5-(4'-vinyl)phenyltetrazole and styrene (eq 1, carbon elemental analyses).

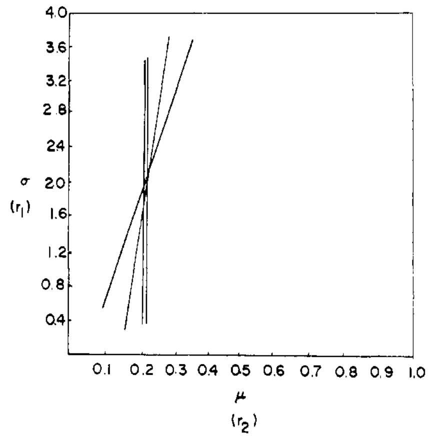

Figure 5. Reactivity ratio for 2-phenyl-5-(4'-vinyl)phenyltetrazole and vinylidene chloride (eq 1, carbon elemental analyses).

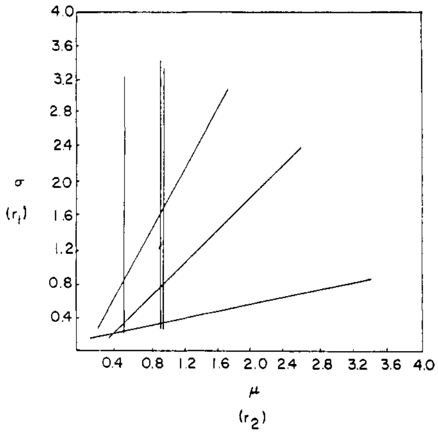

Figure 6. Reactivity ratio for 2-phenyl-5-(4'-vinyl)phenyltetrazole and methyl methacrylate (eq 1, carbon elemental analyses).

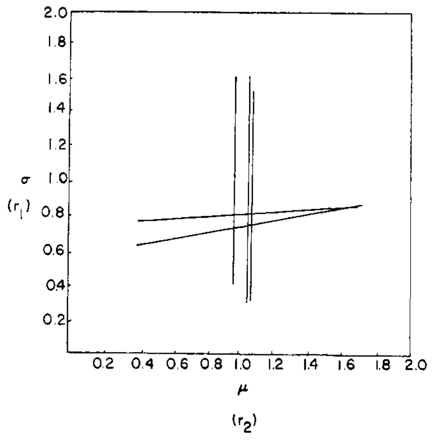

Figure 7. Reactivity ratio for 2-phenyl-5-(4′-vinyl)phenyltetrazole and styrene (eq 1, nitrogen elemental analyses).

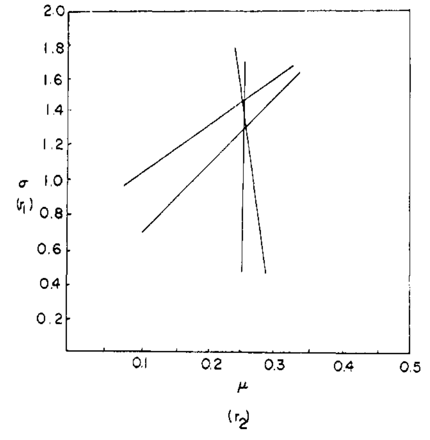

Figure 8. Reactivity ratio for 2-phenyl-5-(4′-vinyl)phenyltetrazole and vinylidene chloride (eq 1, nitrogen elemental analyses).

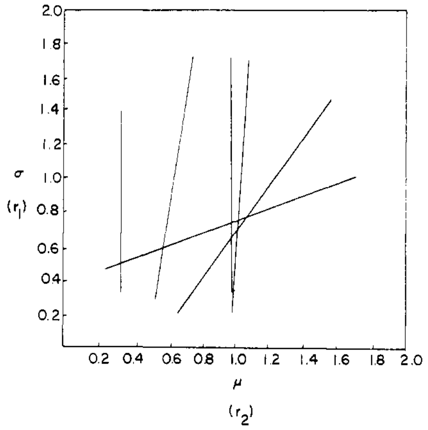

Figure 9. Reactivity ratio for 2-phenyl-5-(4′-vinyl)phenyltetrazole and methyl methacrylate (eq 1, nitrogen elemental analyses).

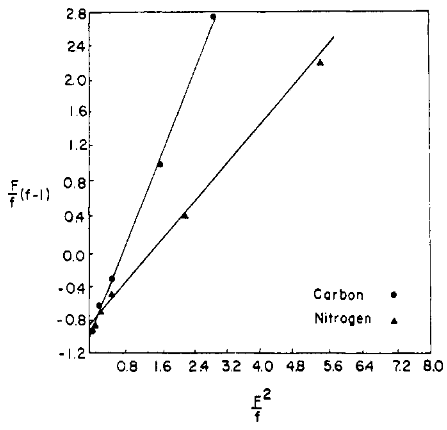

Figure 10. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and styrene (eq 2).

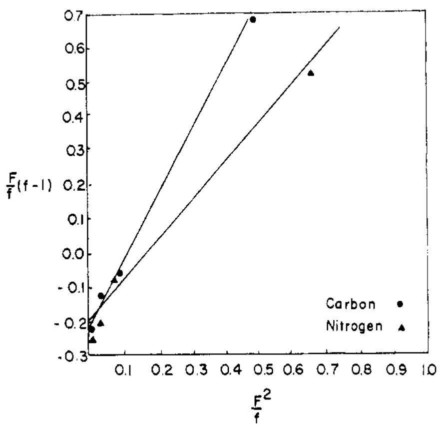

Figure 11. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and vinylidene chloride (eq 2).

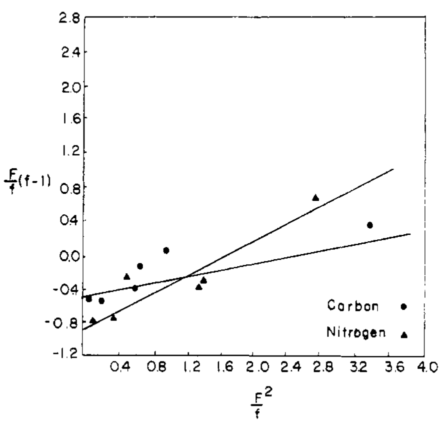

Figure 12. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and methyl methacrylate (eq 2).

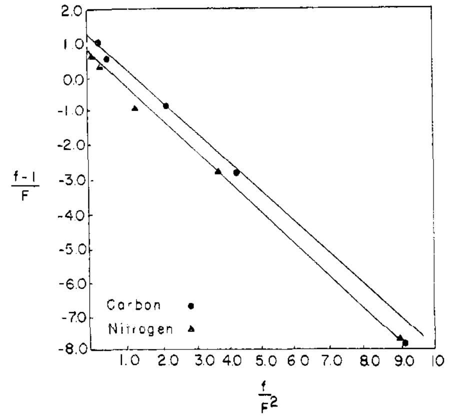

Figure 13. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and styrene (eq 3).

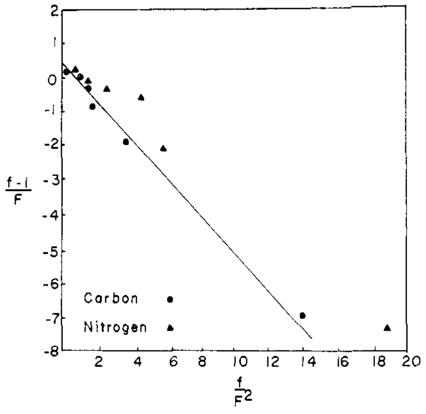

Figure 15. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and methyl methacrylate (eq 3).

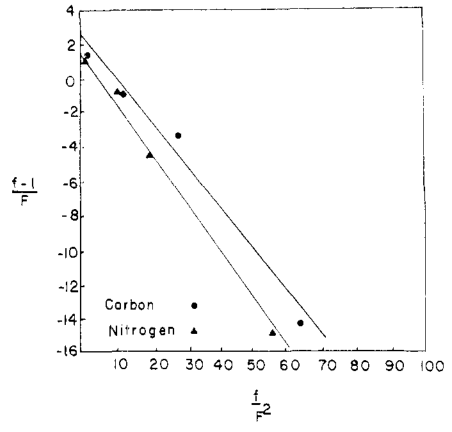

Figure 14. Reactivity ratio of 2-phenyl-5-(4′-vinyl)phenyltetrazole and vinylidene chloride (eq 3).

Experimental Section

Purification of Monomers. The comonomers styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile along with the initiator azodiisobutyronitrile were commercially available reagent grade materials. The four comonomers were each distilled immediately before use. The initiator, azodiisobutyronitrile, was recrystallized from methanol and made up as a stock solution, 4 mg/ml in benzene. The tetrazoylstyrene monomer[2] was recrystallized from Skellysolve C before use.

Free-Radical Homopolymerization of 4-[5′-(2′-Phenyltetrazoyl)]styrene (1). Poly{4-[5′-(2′-phenyltetrazoyl)]-styrene} (2). A solution of 0.506 g (2.00 mmol) of 2-phenyl-5-(4′-vinyl)phenyltetrazole and 1 mg of azodiisobutyronitrile in 5 ml of benzene was sealed in a glass polymerization tube. The tube was immersed in a constant-temperature bath at 60° for 48 hr. The tube was opened and poured into rapidly stirred methanol. A white solid precipitated which was filtered and dried *in vacuo* at 80° to afford 0.36 g (68.3%) of white polymer **2**.

Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.58; H, 4.83; N, 22.58. Found: C, 71.84; H, 4.70; N, 21.45.

Free-Radical Copolymerizations. The free-radical copolymerizations of 2-phenyl-5-(4′-vinyl)phenyltetrazole with styrene, vinylidene chloride, methyl methacrylate, and acrylonitrile were carried out in the same general manner. A typical polymerization which yielded polymer **3** was run as follows. A mixture of 0.770 g (3.10 mmol) of 2-phenyl-5-(4′-vinyl)phenyltetrazole and 0.179 g (1.72 mmol) of styrene along with 5.0 ml of benzene and 1.0 ml of initiator solution was placed in a 20-ml polymerization tube. The contents of the tube were degassed by several freeze–thaw cycles at liquid nitrogen temperature and then sealed *in vacuo*. The tube was immersed in an oil bath at 60.0° and heated for 2 hr. After that time, the tube was removed

TABLE III
SOLUTION COPOLYMERIZATION OF 2-PHENYL-5-(4′-VINYL)PHENYLTETRAZOLE AND STYRENE AT 60° (SEE FIGURES 4, 7, 10, AND 13)

No.	Charge,[a] g (mmol): 2-Phenyl-5-(4′-vinyl)-phenyltetrazole	Charge,[a] g (mmol): Styrene	Time, min	Convn, %	Anal., %[b]: C	Anal., %[b]: N
1	0.770 (3.10)	0.179 (1.72)	140	6.63	73.99	20.05
2	0.609 (2.46)	0.519 (4.99)	180	9.99	77.45	16.24
3	0.387 (1.56)	0.636 (6.11)	175	6.25	79.91	13.21
4	0.999 (4.03)	0.112 (1.08)	130	9.80	73.35	21.21
5	0.250 (1.01)	0.948 (9.10)	250	6.76	84.64	8.79

[a] Solvent, 6 ml of benzene; initiator, 4 mg of azodiisobutyronitrile. [b] The values reported are averages of duplicate determinations.

TABLE IV

SOLUTION COPOLYMERIZATION OF 2-PHENYL-5-(4′-VINYL)PHENYLTETRAZOLE AND VINYLIDENE CHLORIDE AT 60°
(SEE FIGURES 5, 8, 11, AND 14)

No.	Charge,[a] g (mmol)		Time, min	Convn, %	Anal., %[b]	
	2-Phenyl-5-(4′-vinyl)-phenyltetrazole	Vinylidene chloride			C	N
1	0.788 (3.18)	0.274 (2.83)	120	4.11	64.86	20.86
2	0.373 (1.50)	0.578 (5.97)	180	3.79	64.92	18.44
3	0.304 (1.22)	0.853 (8.80)	330	3.77	61.20	16.29
4	0.192 (0.52)	0.912 (9.41)	330	3.04	52.24	12.20

[a] Solvent, 6 ml of benzene; initiator, 4 mg of azodiisobutyronitrile. [b] The values reported are averages of duplicate determinations.

TABLE V

SOLUTION COPOLYMERIZATION OF 2-PHENYL-5-(4′-VINYL)PHENYLTETRAZOLE AND METHYL METHACRYLATE AT 60°
(SEE FIGURES 7, 9, 12, AND 15)

No.	Charge,[a] g (mmol)		Time, min	Convn, %	Anal., %[b]	
	2-Phenyl-5-(4′-vinyl)-phenyltetrazole	Methyl methacrylate			C	N
1	0.751 (3.03)	0.304 (3.04)	180	8.72	70.77	18.19
2	0.696 (2.80)	0.515 (5.15)	180	9.60	69.43	17.91
3	0.782 (3.15)	0.156 (1.56)	180	9.72	71.11	20.37
4	0.481 (1.94)	0.600 (6.00)	150	5.75	68.86	15.29
5	0.746 (3.00)	0.418 (4.18)	120	5.11	70.30	18.19
6	0.251 (1.01)	0.906 (9.06)	180	8.00	66.56	10.01

[a] Solvent, 6 ml of benzene; initiator, 4 mg of azodiisobutyronitrile. [b] The values reported are averages of duplicate determinations.

from the bath, immediately cooled to liquid nitrogen temperature, and opened. The contents of the tube were poured into 200 ml of rapidly stirred methanol. The precipitated white polymer was filtered, dried *in vacuo*, and weighed. The polymer weighed 0.066 g which represents a 6.63% conversion. The polymer was dissolved in benzene, reprecipitated into methanol, filtered, and dried *in vacuo*. The white polymer was dissolved in 3 ml of benzene and poured into a 1-dram sample vial. The sample was frozen, lyophilized, and analyzed for carbon and nitrogen in duplicate (Tables III–V).

Pyrolysis of 2-Phenyl-5-(4′-vinyl)phenyltetrazole–Acrylonitrile Copolymer (6). A solution of 0.250 g of copolymer **6** (30 mol % **2**) in 10 ml of 1,2,4-trichlorobenzene was heated 1 hr at the reflux temperature. A precipitate appeared immediately on heating the solution as the temperature rose above 160° and further precipitate was not formed after ~20 min. The solution was cooled and the brown polymer was filtered and dried *in vacuo* at 212° to give 0.235 g (98%) of product. The polymer was insoluble in formic acid, sulfuric acid, dimethylformamide, hexamethylphosphoramide, 1,2,4-trichlorobenzene, chlorobenzene, and benzene.