son of the CD spectra of the D enantiomer of PCMP in TFE and in TFE-perchloric acid suggests that in TFE a weak negative band might be covered by the strong maximum around 210 m $\mu$  (Figure 3). This band would disappear on addition of perchloric acid, as does the 228-mµ band in poly-(L-proline).<sup>16,21</sup> In the case of poly(L-proline) the addition of a strong acid to the TFE solution of the polymer affects the formation of the disordered form.<sup>16,21</sup> Viscosity measurements suggest a similar conformational transition (Table III) for PCMP. Viscosity measurements in TFE were not possible, because only sample 1 was completely soluble in this solvent. A good solvent system for the viscosity measurements was mixtures of chloroform and methanol. In this system the intrinsic viscosity is of the same magnitude as in DCA (Table III). The addition of lithium bromide to the chloroform-methanol system leads to a drastic decrease of the intrinsic viscosity. Comparable low viscosity values are obtained for TFE-perchloric acid and lithium perchlorate in methanol. This is in accordance with the results for poly(Lproline), which exists in these two solvents in the disordered form, characterized by a low intrinsic viscosity.<sup>21</sup> We therefore tentatively assume a poly(proline II)-type left-handed helix for poly(cis-5-methyl-L-proline) in TFE, methanolchloroform mixtures, and strong acids such as dichloroacetic acid and methanesulfonic acid. For PCMP in salt solutions and in TFE-perchloric acid we assume a disordered form similar to poly(L-proline) in concentrated salt solutions.<sup>8-10</sup>

Although the viscosity measurements clearly indicate solvent-dependent conformational changes, all CD spectra are very similar. They show a negative maximum at higher and a positive maximum at lower wavelength. We assign these two maxima to the split  $\pi - \pi^*$  transition of the amide group. The fact that this splitting occurs in solvents which favor the helical form as well as in solvents which favor the disordered form indicates that in the disordered form a short-range local order is maintained, thus allowing exciton coupling and splitting of the amide transition. Studies on proline oligomers have shown that a trimer or tetramer or proline is sufficient to show this splitting. In this connection it is of interest to note that calculations by Rosenheck<sup>18</sup> predict a parallel exciton band at 209 m $\mu$  and an antiparallel band at 191 m $\mu$ for poly(L-proline). These values are in good agreement with our results on PCMP, although for poly(L-proline) only CD bands at 207 and 228 m $\mu$  have been observed.

The CD spectrum in methanesulfonic acid is red shifted in comparison with the spectrum in TFE, while the uv spectrum is shifted to the blue. This might be due to a protonation of the amide group.<sup>25-29</sup>

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# Synthesis and Copolymerization of Styryl-Substituted Tetrazoles. Thermal Cross-Linking of Copolymers Containing Dipolarophiles and the Tetrazoles as Nitrile Imine Dipole Precursors

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ABSTRACT: The syntheses of six new monomers (1-6) which contain both tetrazole and styrene moieties have been carried out. These monomers have been copolymerized with styrene, vinylidene chloride, and acrylonitrile by free-radical initiation. Reactivity ratios and Q and e values for these monomers were calculated from their elemental and thermogravimetric analysis data. Synthetic elastomeric polymers containing a few per cent of one of these monomers were prepared either by emulsion copolymerizations (SBR type), or by anionic block copolymerizations (natural rubber type). Thermal cross-linking of these copolymers and terpolymers through the 1,3-dipole addition of the nitrile imine, generated from the tetrazole pendant group, across the unsaturation in the polymer has been studied.

The concerted symmetry-allowed thermal [4 + 2] cycloaddition of a 1,3-dipole to a dipolarophile has been employed as one of the chemical reactions in the cross-linking of polymers. For example, compounds such as bifunctional nitrones,<sup>2,3</sup> nitrile oxides,<sup>4,5,6</sup> sydnones,<sup>7,8</sup> and nitrile imines<sup>9</sup>

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(4) J. Hayashi, J. Furukawa, and S. Yamashita, Nippon Gomu Kyokaishi, 43, 313, 358, 807, 818 (1970). have been found to be effective. In curing polymers, the ability to carefully control the degree of cross-linking is desirable; the cross-linking of polymers by initiation of the

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reaction of built-in cross-linking sites along the polymer chain is one of the best ways to achieve this goal.

The thermal decomposition of tetrazoles generates 1,3dipolar nitrile imines which are highly reactive and are capable of reacting with a variety of dipolarophiles to afford excellent yields of cycloaddition products. A monomer



having both styryl and tetrazoyl functional groups can be easily incorporated into many polymers by a copolymerization reaction through the styryl moiety. The copolymer thus formed contains the tetrazole pendant groups along the polymer chain, and the thermal decomposition of these tetrazole units in a copolymer which also contains dipolarophiles pro-



vides a means for cross-linking. Such a cross-linking reaction has been effected in this way by incorporation of a styryl-substituted tetrazole with an acrylonitrile polymer.<sup>10</sup>

It is also valuable in the cross-linking reaction to be able to exercise some degree of control as to the temperature at which it takes place. A Hammett correlation of the rates of thermal decomposition of 2,5-disubstituted tetrazoles reveals that the groups on the 2 position of the tetrazole ring, which in the transition state can delocalize an incipient negative charge, and those on the 5 position, which tend to stabilize an incipient positive charge, increase the rate of decomposition.<sup>11</sup> This is in accord with a transition state which has some of the character of the dipole 7c. From this it was evident that the decomposition temperature of the tetrazole could be varied by changing the electronic nature of the substituents on the 2 and 5 positions.

## Discussion

Six styryl-substituted tetrazole monomers (1-6) were synthesized.



The syntheses of 2-aryl-5-styryltetrazoles and 2-styryl-5aryltetrazoles were carried out by the general procedure shown in Scheme I.

Since alkyl-substituted tetrazoles are readily synthesized by alkylation of 5-monosubstituted tetrazoles, this was the method of choice for the preparation of 2-methyl-5-(4'-vinyl)phenyltetrazole (Scheme II).

The styryl-substituted tetrazoles were expected to have copolymerization characteristics similar to those of styrene. A series of copolymerizations of monomer 1, 2, and 6 with styrene, vinylidene chloride, and acrylonitrile were carried out. These copolymerization reactions were purposely stopped at less than 10% conversion; therefore, it could be assumed that there were no significant changes in the relative monomer concentration from the initial charge. Elemental analysis data of each copolymer were used to calculate the relative amount of each monomer present in that copolymer.

Because the copolymerization reactions were carried out under free-radical conditions, the tetrazole rings in these styryl-substituted tetrazoles remained intact. Quantitative. thermogravimetric analyses on the copolymers not only showed the decomposition temperatures of the tetrazole ring

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	TABLE I	
THE REACTIVITY RATIOS AND (	O AND <i>e</i> VALUES OF STYRYL-SUBSTI	TUTED TETRAZOLES

M <sub>1</sub>	M <sub>2</sub>	$r_1$	$r_2$	, Q	е
1	Styrene	1.9	0.38	2.3	-0.8
2	Styrene	2.2	0.48	2.2	-0.8
	Vinylidene chloride	1.9	0.11	2.2	-1.0
	Acrylonitrile	1.4	0.32	2.5	-1.3
6	Styrene	1.3	0.65	1.4	-0.8
	Vinylidene chloride	1.9	0.13	2.0	-1.0
	Acrylonitrile	1.1	0.42	1.6	-1.2
	Styrene	1.0	0.95	0.90	-0.6
$CH_2 = CH (\bigcirc -C^{\sim} N - C_8H_3)$	Vinylidene chloride	1.8	0.25	0.65	-0.5
N=N	Methyl methacrylate	0.4	0.70	0.70	-0.7

<sup>a</sup> Structure 26; see ref 10.

Scheme I Synthesis of 2-(4'-Vinyl)phenyl-5-aryltetrazole





and of the copolymers themselves, but also showed the amounts of nitrogen lost when the tetrazole units underwent

Scheme II Syntheses of 2-Methyl-5-(4'-vinyl)phenyltetrazole



thermal decomposition. The amounts of nitrogen lost were also used to calculate the composition of copolymers, and compositions calculated from thermogravimetric analyses data were close to those calculated from elemental analyses.

The reactivity ratios and Q and e values for monomer 1, 2, and 6 were calculated from the analytical data on their copolymers, by the use of the integrated copolymerization equation<sup>12</sup> and both forms of the Fineman-Ross equation.<sup>13</sup> These values are summarized in Table I.

These styryl-substituted tetrazoles have r values close to those exhibited by styrene in its copolymerization with the same vinyl monomers. The Q and e values are close to those of styrene, as was expected. The radical associated with the growing styryl-substituted tetrazole appears to be more stable (greater delocalization energy) than that associated with the styrene. A similar result for 2-phenyl-5-(4'-vinyl)phenyltetrazole was reported previously.<sup>10</sup>

The decomposition temperatures of monomers 1-6 and of 2-phenyl-5-(4'-vinyl)phenyltetrazole were determined by

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thermogravimetric analyses. The results are summarized in Table II. The results showed that electron-withdrawing groups on the 2-phenyl (*N*-phenyl) group of the tetrazolring lowered the decomposition temperature, while electrone donating groups raised the decomposition temperature. On the other hand, an opposite trend was observed for the substituents on the 5-phenyl (*C*-phenyl) group, where the electron-withdrawing groups raised the decomposition temperature and the electron-donating groups lowered the decomposition temperature.

Thus, copolymers that contain both tetrazole moieties as nitrile imine dipole precursors and dipolarophiles such as olefins, acetylenes, nitriles, or carbonyl groups can be thermally cross-linked, and the temperature that initiates these cross-linking reactions can be controlled by changing the electronic properties of the substituents on the tetrazole moieties.

Styryl-substituted tetrazole monomers, when initiated by organolithium compounds or by sodium metal under anionic polymerization conditions, were found to afford living polymers. Evidence that living polymers could be obtained was provided by the usual molecular weight increase experiments and syntheses of block polymers.

A block copolymer (25) of 2 and isoprene was prepared by the *n*-butyllithium initiation of isoprene followed by the addition of 2 such that the molar ratio of isoprene to 2 was 50:1. Although the presence of 2 in the copolymer interfered with some of the characteristic absorptions of polyisoprene in the infrared region, it was evident that no trans-1,4 structure was present. The isoprene block consisted of about 95% cis-1,4 and 8% 3,4 structure. Macromolecules

THREE-COMPONENT EMULSION POLYMERIZATION O
2-(4'-VINYL)PHENYL-5-PHENYLTETRAZOLE (2),
STYRENE, AND BUTADIENE

Expt no.	Monomers	Initial <sup>a</sup> monomer comp	← Polyme Calcdª	er comp Found <sup>a</sup>
1	2	4.0	7.01	7.73
	Styrene	27.1	21.60	
	Butadiene	60.0	71.39	
2	2	4.9	8.54	9.51
	Styrene	26.8	21.56	
	Butadiene	68.3	70.20	

<sup>a</sup> Expressed as wt %.



The emulsion copolymerization of 2, styrene, and butadiene was carried out, using a standard "hot" rubber recipe,<sup>14</sup> to prepare samples with different compositions. The anticipated compositions of the SBR samples prepared were calculated following a known method.<sup>15</sup> Q and e values of 2 were obtained from the binary copolymerization of this monomer and other vinyl monomers, and the known Q and e values for styrene and butadiene<sup>16</sup> were used for these two components. Fair agreement between calculated and experimental results of these samples were obtained. The results are shown in Table III.

Copolymers of 2 with isoprene, acrylonitrile, or butadiene, whether they were prepared by free-radical copolymerizations in the solution, by emulsion copolymerizations, or by anionic block copolymerizations, underwent rapid cross-linking at around 200°. The SBR-type terpolymers of 2, styrene, and butadiene could be thermally cross-linked with a high crosslinking efficiency (>90%) to afford elastomers with physical properties comparable to those of regular SBR elastomers cured by conventional sulfur and zinc oxide methods.<sup>17</sup>

#### **Experimental Section**

Monomer. 2-*p*-Tolyl-5-phenyltetrazole (12b). To a mixture of 15.5 g (0.675 g-atom) of sodium metal and 210 ml of ethylene glycol monomethyl ether was added slowly 35.0 g(0.168 mol) of benzaldehyde-*p*-tolylhydrazone.<sup>18</sup> This mixture was heated to  $110^{\circ}$  and 20.3 g (0.17 mol) of phenyl azide was added dropwise. After the addition was complete, the reaction mixture was heated at  $110^{\circ}$ 

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					Analyse	s, <sup>1</sup> %——
Read	ctants, mol	Tetrazole	Yield, % mp, °C	Nmr δ	Calcd	Found
A	0.079ª	2-(4'-Methyl)phenyl-5-	35.4	2.39 <sup>i</sup> (s, 3 H)	C, 67.67	67.61
В	0.087	(4'-methoxyl)phenyl-	108-109 <sup>h</sup>	3.82 (s, 3 H)	H, 5.26	5.22
		tetrazole (12a)		6.83-8.16 (m, 8 H)	N, 21.05	20.67
Α	0.168 <sup>b</sup>	2-(4'-Methyl)phenyl-5-	45.0	$2.44^{i}$ (s, 3 H)	C, 71.20	71.31
В	0.170	phenyltetrazole (12b)	105-106°	7.20-8.30 (m, 9 H)	H, 5.09	5.07
		• • • • •			N, 23.71	22.64
Α	0.021°	2-(4'-Methyl)phenyl-5-	64.6	2.41 <sup><i>i</i></sup> (s, 3 H)	C, 68.97	68.86
В	0.023	(4'-cyano)phenyltetrazole	167–169 <sup>h</sup>	7.41-8.39 (m, 8 H)	H, 4.21	4,42
		(12c)			N, 26.82	26.61
Α	0.061ª	2-(4'-Chloro)phenyl-5-	53.6	2.38 <sup>i</sup> (s, 3 H)	C, 62.22	62.14
В	0.070	(4'-methyl)phenyltetrazole	143-144 <sup>h</sup>	7.28-8.19 (m, 8 H)	H, 4.07	4.24
		(13d)			N, 20.74	20.17
Α	0.014	2-(4'-Methoxyl)phenyl-5-	51.0	2.39 <sup>i</sup> (s, 3 H)	C, 67.67	67.89
В	0.016	(4'-methyl)phenyltetrazole	112–113 <sup>h</sup>	3.83 (s, 3 H)	H, 5.26	5.14
		(13e)		6.93-8.19 (m, 8 H)	N, 21.05	20.85

 TABLE IV

 PREPARATION OF TETRAZOLES.
 REACTIONS OF HYDRAZONES (A) WITH PHENYL AZIDE (B)

<sup>a</sup> 4-Methoxylbenzaldehyde-*p*-tolylhydrazone (10a), mp 132–133°. <sup>b</sup> Benzaldehyde-*p*-tolylhydrazone (10b), mp 118–119°. <sup>c</sup> 4-Cyanobenzaldehyde-*p*-tolylhydrazone (10c), mp 153–154°. <sup>d</sup> *p*-Tolylaldehyde-4-chlorophenylhydrazone (9d), mp 160–161°. <sup>e</sup> *p*-Tolylaldehyde-5methoxylphenylhydrazone (9e), mp 135–136°. <sup>f</sup> Analyses were made on a F&M Scientific Model 185 carbon, hydrogen, nitrogen analyzer. <sup>e</sup> Recrystallized from methanol. <sup>h</sup> Recrystallized from 95% ethanol. <sup>i</sup> Carbon tetrachloride as solvent. <sup>j</sup> Deuterated chloroform as solvent.

Read	ctants, mol	Monobromides	Yield, % mp, °C	Nmr δ	Analyse Calcd	es, <sup>g</sup> % Found
	0.015	2 (4) Promonethally hand	06.0	2 70; (- 2 11)		51.00
A	0.013	2-(4 -Bromomethyl)phenyl-	90.9	3. /9° (S, 3 H)	C, 52.17	51.90
В	0.019	5-(4'-methoxyl)phenyl-	125-126 <sup>n</sup>	4.43 (s, 2 H)	H, 3.77	3.51
		tetrazole (14a)		6.62-8.21 (m, 8 H)	N, 16.23	16.05
Α	$0.148^{b}$	2-(4'-Bromomethyl)phenyl-	98.0	$4.50^{i}$ (s, 2 H)	C, 53.41	53.02
В	0.150	5-phenyltetrazole (14b)	136-138 <sup>h</sup>	7.21-8.30 (m, 9 H)	H, 3.49	3.20
					N, 17.79	18.01
Α	0.034°	2-(4'-Bromomethyl)phenyl-	85.0	4.53 <sup>i</sup> (s, 2 H)	C, 52.95	52.18
В	0.034	5-(4'-cyano)phenyl-	173–175 <sup>h</sup>	7.28-8.43 (m, 8 H)	H, 2.94	3.10
		tetrazole (14c)			N, 20.59	19.97
Α	0.035ª	2-(4'-Chloro)phenyl-5-	93.1	$4.52^{i}$ (s, 2 H)	C, 48.14	48.31
В	0.036	(4'-bromomethyl)phenyl-	137–138 <sup>h</sup>	7.26-8.27 (m, 8 H)	H, 2.87	3.17
		tetrazole (15d)			N, 16.12	15.48
Α	0.072*	2-(4'-Methoxyl)phenyl-5-	98.2	$3.84^i$ (s, 3 H)	C, 52.17	52.54
В	0.072	(4'-bromoethyl)phenyl-	128-129 <sup>h</sup>	4.49 (s, 2 H)	H, 3.77	4.07
		tetrazole (15e)		6.91-8.25 (m, 8 H)	N, 16.23	15.48
Α	0.130/	2-Methyl-5-(4'-bromo-	91.0	$4.42^{i}$ (s, 3 H)	C, 42.70	42.86
В	0.130	methyl)phenyltetrazole (22)	$114 - 115^{h}$	4.78 (s, 2 H)	H, 3.56	3.83
				7.49-8.11 (m, 4 H)	N, 22.15	22.13

 TABLE V

 PREPARATION OF MONOBROMIDES.
 REACTIONS OF TETRAZOLES (A) WITH N-BROMOSUCCINIMIDE (B)

<sup>a</sup> 2-(4'-Methyl)phenyl-5-(4'-methoxyl)phenyltetrazole (12a). <sup>b</sup> 2-(4'-Methyl)phenyl-5-phenyltetrazole (12b). <sup>c</sup> 2-(4'-Methyl)phenyl-5-(4'-cyano)phenyltetrazole (12c). <sup>d</sup> 2-(4'-Chloro)phenyl-5-(4'-methyl)phenyltetrazole (13d). <sup>e</sup> 2-(4'-Methoxyl)phenyl-5-(4'-methyl)phenyltetrazole (13e). <sup>f</sup> 2-Methyl-5-p-tolyltetrazole (21). <sup>e</sup> Analyses were made on a F&M scientific Model 185 carbon, hydrogen, nitrogen analyzer. <sup>h</sup> Recrystallized from 95% ethanol. <sup>f</sup> Deuterated chloroform as solvent.

for 4 hr. It was then cooled in an ice-water bath and 200 ml of 2 N hydrochloric acid was added. The gray crystals were filtered and washed with cold methanol. Recrystallization from methanol gave white needles (17.8 g, 0.076 mol, 45%): mp 105–106; nmr (CCl<sub>4</sub>)  $\delta$  2.44 (s, 3 H, methyl), 7.20–8.30 (m, 9 H, phenyl). *Anal.* Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>: C, 71.20; H, 5.09; N, 23.71. Found: C, 71.31; H, 5.07; N, 22.64.

Other tetrazoles were prepared according to a similar procedure a described above. The details of those syntheses are summarized in Table IV.

**2-(4-Bromomethyl)phenyl-5-phenyltetrazole (14b).** A solution of 35.0 g (0.148 mol) of 2-*p*-tolyl-5-phenyltetrazole and 26.7 g (0.150 mol) of *N*-bromosuccinimide in 450 ml of dry carbon tetrachloride was heated at the reflux temperature. After the mixture had started refluxing, 0.1 g of benzoyl peroxide was added. The reaction mix-

ture was heated at the reflux temperature for 8 hr and another portion of 0.1 g of benzoyl peroxide was added after the fourth hour. The mixture was then filtered hot to remove the succinimide. On cooling the filtrate, 2-(4'-bromomethyl)phenyl-5-phenyltetrazole was obtained as pale yellow crystals. Recrystallization from carbon tetrachloride gave white crystals (44.5 g, 0.145 mol, 98%): mp 136-138°; nmr (CDCl<sub>3</sub>),  $\delta$  4.5 (s, 2 H, methylene), 7.20-8.31 (m, 9 H, phenyl). *Anal.* Calcd for C<sub>14</sub>H<sub>11</sub>N<sub>4</sub>Br: C, 53.41; H.3.49; N, 17.79. Found: C, 53.02; H, 3.20; N, 18.01.

Other monobromides were prepared according to a similar procenure as described above. The details of these syntheses are summarized in Table V.

**2-(4'-Dibromomethyl)phenyl-5-phenyltetrazole (16b).** A mixture of 44.5 g (0.145 mol) of 2-(4'-bromomethyl)phenyl-5-phenyltetrazole and 26.8 g (0.150 mol) of *N*-bromosuccinimide in 450 ml of

					Analyse	es,º %
Read	ctants, mol	Dibromides	Yield, % mp, °C	Nmr δ	Calcd	Found
Α	0.016ª	2-(4'-Dibromomethyl)-	92.0	3.85 <sup>i</sup> (s, 3 H)	C, 42.45	41.75
В	0.019	phenyl-5-(4'-methoxyl)-	120–121 <sup>h</sup>	6.65 (s, 1 H)	H, 2.83	2.39
		phenyltetrazole (16a)		6.88-8.29 (m, 8 H)	N, 13.21	12.81
Α	0.1455	2-(4'-Dibromomethyl)-	75.2	$6.77^{i}$ (s, 1 H)	C, 42.62	41.73
В	0.151	phenyl-5-phenyltetrazole	112–114 <sup>h</sup>	7.20-8.30 (m, 9 H)	H, 2.54	2.52
		(16b)			N, 14.21	13.46
Α	0.034°	2-(4'-Dibromomethyl)-	61.0	$6.69^i$ (s, 1 H)	C, 42.96	42.98
В	0.034	phenyl-5-(4'-cyano)-	163–165 <sup>h</sup>	7.28-8.41 (m, 8 H)	H, 2.15	3.01
		phenyltetrazole (16c)			N, 16.71	16.89
Α	0.030 <sup>d</sup>	2-(4'-chloro)phenyl-5-	90.8	$6.63^i$ (s, 1 H)	C, 39.25	39.61
В	0.032	(4'-dibromomethyl)	$117 - 118^{h}$	7.41-8.26 (m, 8 H)	H, 2.10	1.95
		phenyltetrazole (17d)			N, 13.08	13.60
Α	0.070°	2-(4'-Methoxyl)phenyl-5-	95.0	$6.68^i$ (s, 1 H)	C, 42.45	41.70
В	0.070	(4'-dibromomethyl)-	109–110 <sup>h</sup>	6.92-8.29 (m, 8 H)	H, 2.83	2.60
		phenyltetrazole (17e)		3.87 (m, 3 H)	N, 13.21	12.51
Α	0.132/	2-Methyl-5-(4'-dibromo-	47.0	$4.42^{i}$ (s, 3 H)	C, 32.51	32.25
В	0.135	methyl)phenyltetrazole	$104 - 105^{h}$	7.49 (s, 1 H)	H, 2.01	2.42
		(23)		7.72-8.10 (m, 4 H)	N, 16.88	16.09

 TABLE VI

 PREPARATION OF DIBROMIDES.
 REACTIONS OF MONOBROMIDES (A) WITH N-BROMOSUCCINIMIDE (B)

<sup>a</sup> 2-(4'-Bromomethyl)phenyl-5-(4'-methoxyl)phenyltetrazole (14a). <sup>b</sup> 2-(4'-Bromomethyl)phenyl-5-phenyltetrazole (14b). <sup>c</sup> 2-(4'-Bromomethyl)phenyltetrazole (15d). <sup>e</sup> 2-(4'-Methoxyl)phenyl-5-(4'-bromomethyl)phenyltetrazole (15d). <sup>e</sup> 2-(4'-Methoxyl)phenyl-5-(4'-bromomethyl)phenyltetrazole (15d). <sup>e</sup> 2-(4'-Methoxyl)phenyl-5-(4'-bromomethyl)phenyltetrazole (15d). <sup>e</sup> 2-(4'-Methoxyl)phenyltetrazole (15d). <sup>e</sup> 2-(4'-Methoxyltetrazole (15d)

TABLE VII	
PREPARATION OF SUBSTITUTED TETRAZOYLBENZALDEHYDE.	HYDROLYSIS OF DIBROMIDES

				Analyse	es, <sup>g</sup> %
Reactants, mol	Tetrazoylbenzaldehydes	Yield, % mp, °C	Nmr δ	Calcd	Found
0.013a	4-(2'-(5'-(4'-Methoxyl-	84.2	3.80 <sup>i</sup> (s, 3 H)	C, 64.29	64.50
	phenyl)tetrazoyl)benz-	128–129 <sup>h</sup>	6.97-8.34 (m, 8 H)	H, 4.29	3.96
	aldehyde (18a)		10.00 (s, 1 H)	N, 20.00	19.76
$0.103^{b}$	4-(2'-(5'-Phenyltetrazoyl))-	72.8	7.50-8.33 <sup>i</sup> (m, 9 H)	C, 67.25	67.32
	benzaldehyde (18b)	130-131 <sup>h</sup>	10.00 (s, 1 H)	H, 4.01	4.07
				N, 22.43	22.70
0.018°	4-(2'-(5'-(4'-Cyanophenyl)-	34.8	7.33-8.47 <sup>i</sup> (m, 8 H)	C, 65.45	66.05
	tetrazoyl))benzaldehyde	166–168 <sup>h</sup>	10.03 (s, 1 H)	H, 3.27	3.45
	( <b>18c</b> )			N, 25.45	24.91
0.027 <sup>d</sup>	4-(5'-(2'-(4'-Chlorophenyl)-	82.9	7.52-8.27 <sup>i</sup> (m, 8 H)	C, 59.15	58.78
	tetrazoyl))benzaldehyde	137–138 <sup>h</sup>	10.02 (s, 1 H)	Н, 3.17	3.46
	( <b>19d</b> )			N, 19.72	18.91
0.059*	4-(5'-(2'-(4'-Methoxy-	$74.0^{h}$	3.84 <sup>i</sup> (s, 3 H)	C, 64.29	63.76
	phenyl)tetrazoyl))benz-	162-163	6.90-8.40 (m, 8 H)	H, 4.29	4.38
	aldehyde (19e)		10.00	N, 20.00	19.46
0.060/	4-(5'-(2'-Methyltetrazoyl))-	93.0 <sup>h</sup>	9.99 <sup>i</sup> (s, 1 H)	C, 57.45	57.63
	benzaldehyde (24)	134-135	4.42 (s, 3 H)	H, 4.26	4.42
			7.90-8.17 (m, 4 H)	N, 29.80	28.94

<sup>*a*</sup> 2-(4'-Dibromomethyl)phenyl-5-(4'-methoxyl)phenyltetrazole (16a). <sup>*b*</sup> 2-(4'-Dibromomethyl)phenyl-5-phenyltetrazole (16b). <sup>*c*</sup> 2-(4'-Dibromomethyl)phenyl-5-(4'-chloro)phenyl-5-(4'-dibromomethyl)phenyltetrazole (17d). <sup>*c*</sup> 2-(4'-Methoxyl)phenyltetrazole (17e). <sup>*t*</sup> 2-Methyl-5-(4'-dibromomethyl)phenyltetrazole (23). <sup>*e*</sup> Analyses were made on a F&M Scientific Model 185 carbon, hydrogen, nitrogen analyzer. <sup>*h*</sup> Recrystallized from 95% ethanol. <sup>*i*</sup> Deuterated chloroform as solvent.

dry carbon tetrachloride was heated to the reflux temperature and 0.1 g of benzoyl peroxide was added. The mixture was heated at the reflux temperature for 8 hr, and another portion of 0.1 g of benzoyl peroxide was added after the fourth hour. The insoluble succinimide was then removed from the hot solution; the filtrate was allowed to cool and 2-(4'-dibromomethyl)phenyl-5-phenyl-tetrazole was obtained as light yellow crystals. Recrystallization from carbon tetrachloride gave white crystals (43 g, 0.11 mol, 75%): mp 112–114°; nmr (CDCl<sub>3</sub>),  $\delta$  6.77 (s, 1 H, methine), 7.20–8.30 (m, 9 H, phenyl). Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>Br<sub>2</sub>: C, 42.62; H, 2.54; N, 14.21. Found: C, 41.73; H, 2.52; N, 13.46.

Other dibromides were prepared according to a similar procedure

as described above. The details of these syntheses are summarized in Table VI.

**4-(2'-(5'-Phenyltetrazoyl))benzaldehyde (18b).** A solution of 40.6 g (0.103 mol) of 2-(4'-dibromomethyl)phenyl-5-phenyltetrazole and 46 g (0.250 mol) of potassium oxalate in 750 ml of 70% ethanol was heated at the reflux temperature for 72 hr. The solution was then allowed to cool, and 17 g (0.063 mol) of disodium phosphate heptahydrate was added and the solution was stirred for 1 hr. The precipitate was filtered and discarded. The filtrate was allowed to evaporate to dryness and 4-(2'-(5'-phenyltetrazoyl))-benzaldehyde was obtained as pale yellow crystals. Recrystallization from Skelly C gave white crystals (19.1 g, 0.077 mol, 73%):

Read	tants, mol	Styryl-substituted tetrazoles	Yield. % mp. °C	Nmr δ	Analyse Calcd	es, <sup>a</sup> %—— Found
			, , , , , , ,			
Α	$0.051^{a}$	2-(4'-Vinyl)phenyl-5-	71.2	$3.85^{h}$ (s, 3 H)	<b>C</b> , 69.07	69.07
в	0.097	(4'-methoxy)phenyltetra-	153-154	5.24-6.82 (m, 3 H)	H, 5.04	5.32
		zole (1)		7.07-8.21 (m, 8 H)	N, 20.14	19.88
Α	$0.080^{b}$	2-(4'-Vinyl(phenyl-5-	90.7	5.29-7.14 <sup>h</sup> (m, 3 H)	C, 72.60	72.70
В	0.122	phenyltetrazole (2)	87-87.5	7.59-8.27 (m, 9 H)	H, 4.84	4.86
					N, 22.58	22.22
Α	0.014°	2-(4'-Vinyl(phenyl-5-	42.0	4.59-5.89 <sup>h</sup> (m, 3 H)	C, 70, 33	70.45
В	0.018	(4'-cyano)phenyltetrazole	121-122	7.33-8.43 (m, 8 H)	H, 4.03	4.31
		(3)			N, 25.64	25.42
Α	0.011 <sup>d</sup>	2-(4'-Chloro)phenyl-5-	71.2	5.29-7.09 <sup>h</sup> (m, 3 H)	C, 63.83	63.69
В	0.021	(4'-vinyl)phenyltetrazole	103-104	7.55-8.23 (m, 8 H)	H, 3.90	3.74
		(4)			N, 19.86	19.71
Α	0.130	2-(4'-Methoxy)phenyl-5-	44.8	$5.23-6.73^{h}$ (m, 3 H)	C, 69.07	68.80
В	0.020	(4'-vinyl)phenyltetrazole	81-82	6.96-8.28 (m, 8 H)	H, 5.04	5.31
		(5)		3.87 (s, 3 H)	N, 20.14	20.32
Α	0.055/	2-Methyl-5-(4'-vinyl)-	93.0	$4.42^{h}$ (s, 3 H)	C, 64 52	64.33
В	0.080	phenyltetrazole (6)	61-62	5.27-7.06 (m, 3 H)	H, 5.37	5.43
				7.50-8.12 (m. 4 H)	N. 30.11	29.93

 TABLE VIII

 PREPARATION OF STYRYL-SUBSTITUTED TETRAZOLES. REACTIONS OF TETRAZOYLBENZALDEHYDE (A) WITH

 TRIPHENYLMETHYLPHOSPHONIUM BROMIDE (B)

<sup>a</sup> 4-(2'-(5'-(4'-Methoxyphenyl)tetrazoyl)benzaldehyde (**18a**). <sup>b</sup> 4-(2'-(5'-Phenyltetrazoyl)benzaldehyde (**18b**). <sup>c</sup> 4-(2'-(5'-(4'-Cyanophenyl)tetrazoyl))benzaldehyde (**19b**). <sup>e</sup> 4-(5'-(2'-(4'-Chlorophenyl)tetrazoyl))benzaldehyde (**19c**). <sup>e</sup> 4-(5'-(2'-(4'-Methoxyphenyl)tetrazoyl))benzaldehyde (**19e**). <sup>e</sup> 4-(5'-(2'-Methyltetrazoyl)benzaldehyde (**24**). <sup>e</sup> Analyses were made on a F&M Scientific Model 185 carbon, hydrogen, nitrogen analyzer. <sup>h</sup> Deuterated dimethyl sulfoxide as solvent.

mp 130–130.5°; nmr (CDCl<sub>3</sub>),  $\delta$  7.50–8.33 (m, 9 H, phenyl), 10.01 (s, 1 H, benzal). *Anal.* Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O: C, 67.25; H, 4.01; N, 22.43. Found: C, 67.32; H, 4.07; N, 22.70.

Other tetrazoyl-substituted benzaldehydes were prepared according to a similar procedure as described above. The details of these syntheses are summarized in Table VII.

2-(4'-Vinyl)phenyl-5-phenyltetrazole (2). To 500 ml of liquid ammonia containing a small amount of anhydrous ferric chloride was added 3.45 g (0.150 g-atom) of sodium metal in small portions. The solution was stirred for 1 hr, then 42.9 (0.120 mol) of triphenylmethylphosphonium bromide was added with stirring. The ammonia was then allowed to evaporate. The entire system was placed under an atmosphere of dry nitrogen and 500 ml of ether which had been freshly distilled from lithium aluminum hydride was added. A solution of 19.9 g (0.080 mol) of 4-(2'-(5'-phenyltetrazoyl)benzaldehyde in 500 ml of dry benzene was added to the ether solution of methylenetriphenylphosphorus over a period of 30 min. The solution was stirred for 30 min then filtered, and the solvent was removed under reduced pressure. The residue was placed on a column of 120 g of chromatographic grade alumina which had been packed from a slurry in Skelly C. The column was eluted with 3000 ml of Skelly C. The first 1500 ml from that column was evaporated to dryness under reduced pressure to give white crystals (18 g, 0.073 mol, 91%): mp 87.0-87.5°; nmr (DMSOd<sub>6</sub>), δ 5.29-7.14 (m, 3 H, vinyl), 7.59-8.27 (m, 9 H, phenyl). Anal. Calcd for  $C_{15}H_{12}N_4$ : C, 72.60; H, 4.84; N, 22.58. Found: C, 72.70; H, 4.86; N, 22.22.

Other styryl-substituted tetrazoles were prepared according to a similar procedure as described above. The details of those syntheses are summarized in Table VIII.

**2-Methyl-5**-*p*-tolyltetrazole (21). To a cold solution of 23.5 g (0.147 mol) of 5-*p*-tolyltetrazole<sup>19</sup> and 12 g (0.300 mol) of sodium hydroxide in 50 ml water was added a solution of 20.9 g (0.147 mol) of methyl iodide in 150 ml of acetone. The mixture was heated to the reflux temperature for 1 hr and another portion of 20.9 g (0.147 mol) of methyl iodide in 20 ml of acetone was added. The heating was continued for 3 hr more and the reaction mixture was then cooled and mixed with 250 ml of benzene. The benzene layer was separated and washed with water several times until the

(19) R. M. Herbst and K. R. Wilson, J. Org. Chem., 22, 1124 (1957).

washings were no longer alkaline. The benzene layer was dried over calcium chloride, and then solvent was removed under reduced pressure to afford a pale yellow precipitate. Recrystallization, once from an ethyl ether-benzene mixture (3:1) and once from ethyl ether, gave long thin needles (22.5 g, 0.130 mol, 88%): mp 91-92°; nmr (DMSO- $d_6$ ),  $\delta$  2.37 (s, 3 H, methyl), 4.42 (s, 3 H, *N*methyl), 7.28-8.03 (m, 4 H, phenyl). *Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>: C, 62.05; H, 5.75; N, 32.20. Found: C, 61.98; H, 5.95; N, 31.63.

**Polymerizations. Free-Radical Copolymerizations.** Copolymerizations were carried out as previously described for 2-phenyl-5-(4'-vinyl)phenyltetrazole.<sup>10</sup> Reactivity ratios were calculated on the basis of carbon, nitrogen, and thermogravimetric analyses. Calculations using the integrated copolymer equation and both forms of Fineman-Ross equations were carried out with modified computer programs.<sup>20, 21</sup>

Anionic Polymerizations. (1) The isoprene used in the polymerization was dried over sodium and distilled in a vacuum line into a reservoir coated with a sodium mirror. Partial polymerization was allowed to occur, and the pure monomer was transferred to the reaction vessel by a bulb-to-bulb distillation. The solvents, benzene, toluene, and *n*-heptane, were washed with concentrated sulfuric acid followed by water and then dried over sodium. They were distilled over lithium aluminum hydride immediately before use. Tetrazole monomers were recrystallized several times and stored *in vacuo* over a drying agent.

(2) The homopolymerization of 2-(4'-vinyl)phenyl-5-phenyltetrazole (2) was carried out as follows. To a glass vessel equipped with a breakable seal was added 0.3410 g (1.38 mmol) of 2-(4'vinyl)phenyl-5-phenyltetrazole and 15 ml of *n*-heptane. The vessel was sealed *in vacuo* and attached to a mixing flask. The flask was evacuated and 0.3 ml of 0.1 *M n*-butylithium in *n*-heptane was added. The flask was further evacuated to remove the *n*-heptane and was sealed *in vacuo*. The flask was cooled to  $-78^{\circ}$  and the monomer solution was introduced with stirring. When the addition was complete, the flask was allowed to stand at room tempera-

<sup>(20)</sup> D. R. Montgomery and C. E. Fray, J. Polym. Sci., Part C, No. 25, 59 (1968).

<sup>(21)</sup> S. P. Chang, T. K. Miwa and W. H. Tallent, J. Polym. Sci., 7, 471 (1969).

ture for 12 hr. The flask was opened and the polymer was precipitated into 200 ml of rapidly stirred methanol.

(3) The presence of living polymer of 2-(4'-vinyl)phenyl-5phenyltetrazole was confirmed as follows. Into a glass vessel equipped with a breakable seal (A) was added 0.4633 g (1.87 mmol) of 2-(4'-vinyl)phenyl-5-phenyltetrazole and 15 ml of tetrahydrofuran. To an identical vessel (B) was added 0.5747 g (2.32 mmol) of 2-(4'-vinyl)phenyl-5-phenyltetrazole and 15 ml of tetrahydrofuran. Both vessels A and B were sealed in vacuo and attached to a mixing flask (C). To this flask was also attached an empty glass vessel (D). The flask C was evacuated and 0.25 ml of 0.1 M nbutyllithium in *n*-heptane was added under a nitrogen atmosphere. The flask was further evacuated to remove the *n*-heptane. It was then sealed in vacuo and cooled to  $-78^{\circ}$ . The 2-(4'-vinyl)phenyl-5-phenyltetrazole solution in vessel A was introduced into the flask via a breakseal and stirred for 15 min after the addition was complete. One-fifth of the solution was transferred into the empty vessel D and sealed, and the 2-(4'-vinyl)phenyl-5-phenyltetrazole solution in vessel B was then introduced into the reaction flask C via a breakseal and stirred for 1 hr after the addition was complete. The contents in the reaction flask C and in vessel D were emptied separately into excess methanol. The white polymer was collected, dried in vacuo, and weighed. From vessel D, 0.0604 g of white polymer ( $[\eta] = 0.45$ ,  $M_n = 11,000$ ) was obtained; from the reaction flask C, 0.6529 g of white polymer ( $[\eta] = 0.78$ ,  $M_{\rm p} = 18,000$ ) was obtained.

(4) The copolymerization of 2 with isoprene was carried out as follows. Into a glass vessel equipped with a breakable seal was added 0.2543 g (1.03 mmol) of 2 and 30 ml of n-heptane. To an identical vessel was added 3.405 g (44.8 mol) of isoprene and 10 ml of n-heptane. Both vessels were sealed in vacuo and attached to a mixing flask. After 0.3 ml of 0.1 Mn-butylithium in n-heptane had been introduced into the flask and the heptane had been removed, the flask was sealed in vacuo and cooled to  $-78^{\circ}$ . The solution of isoprene was introduced and stirred for 15 min after the addition was complete. The solution of 2 was then added and after the addition was complete, the reaction mixture was slowly stirred at room temperature for 12 hr. The polymer was then precipitated into 400 ml of rapidly stirred methanol:  $[\eta] = 0.43$ .

Emulsion Polymerization. The emulsion polymerization of 2 was carried out as follows. To 40 ml of deionized water in a pressure bottle was added 1 g of dodecyl sodium sulfate and 0.05 g of potassium persulfate. In 5.5 g (52.9 mmol) of styrene was dissolved 0.8071 g (3.2 mmol) of 2 and 0.1 g of *n*-dodecyl mercaptan. This styrene solution was added to the pressure bottle. This bottle was cooled in an ice-water bath and approximately 18 g of butadiene was added. The excess butadiene was left in the bottle. The bottle was then capped and immersed in a mechanically tumbled constant-temperature bath and heated at 50  $\pm$  1° for 21 hr. It was then cooled and 2 ml of distilled water containing 0.5 g of phenyl- $\beta$ naphthylamine was added. The coagulated polymer was filtered. It was purified by reprecipitation from benzene solution into methanol and dried in vacuo to afford 14.8 g (73%) of rubbery white polymer:  $[\eta] = 0.91$ .

Cross-Linking Reaction. Polymer samples were cross-linked by first determining their decomposition temperatures by tga. Samples were then either heated dry to the appropriate temperature for a few minutes or heated in a solvent with a suitable boiling point at the reflux temperature. Solubility of the polymer which had been cross-linked dry was then tested in a variety of good polymer solvents. In the case of cross-linking in a solvent, precipitation started within minutes.

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# Preparation and Characterization of Four-Branched Star Polystyrene

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ABSTRACT: A method is described for the preparation of well-defined four-star polystyrenes involving coupling of polystyryllithium with 1,2-bis(methyldichlorosilyl)ethane. Nine samples were prepared over a 30-fold range of molecular weight. Osmotic and light-scattering techniques were used to measure number- and weight-average molecular weights where possible. Intrinsic viscosity and sedimentation coefficients were measured in cyclohexane at 35 and 50° and in toluene at 35°. The ratio  $g'([\eta](\text{branched})/[\eta](\text{linear}))$  was found to be 0.76 under  $\theta$  conditions and slightly lower in better solvents. The value falls between theoretical estimates. The corresponding ratio of sedimentation coefficients (h) was found to be 0.93–0.94 compared with a theoretical value of 0.89.

he synthesis of well-defined branched polymers became  $\mathbf{I}$  feasible with the discovery of anionic polymerization systems that are free of chain transfer and termination reactions. Attempts to synthesize star polymers by anionic methods have generally run along two lines. The research group at Mellon Institute treated living polystyryllithium with tri- and tetra(chloromethyl)benzene compounds in a mixture of benzene and tetrahydrofuran.<sup>1,2</sup> Although the desired tri- and tetrafunctional star polymers were obtained in good yield, the presence of higher molecular weight polymer made it particularly difficult to purify them. To avoid higher molecular weight coupling products, larger percentages of tetrahydrofuran and higher temperatures had to be used. Under these conditions polystyryllithium becomes unstable. The use of potassium as the counterion avoids difficulties at the coupling stage but tends to widen the molecular weight distribution of the polymer.3 The same method was used recently with hexa[p-(chloromethyl)phenyl]benzene to produce six-branched star polystyrene.<sup>4</sup>

The second route to star polymers uses the reaction of living polymers with polyfunctional silicon chloride com-

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