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## HIGH TEMPERATURE POLYMERS

### FROM

## 1, 3-DIPOLAR ADDITION REACTIONS

by

J. K. Stille L. D. Gotter M. A. Bedford F. W. Harris

### FINAL REPORT

### 1 February 1965 to 30 June 1968

## CONTRACT NO. DA-11-070-AMC-832 (W) AMC PROJECT NO. 5025.11.84203

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Rock Island Arsenal Rock Island, Illinois 61201



Department of Chemistry The University of Iowa

1968 1968

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U.S. Army Weapons Command Rock Island Arsenal Rock Island, Illinois

### PREFACE

This report w prepared under U.S. Army Contract No. DA-11-070-AMC-832(W). The work was administered under the direction of Rock Island Arsenal, Rock Island, Illinois, with Mr. Z. T. Ossefort acting as Project Officer.

This report covers work conducted from 1 February 1965 to 30 June 1968.

The project personnel were L. D. Gotter, M. A. Bedford and F. W. Harris.

F.K. Stille

J. K. Stille Professor Organic Chemistry Principal Investigator 30 June 1968

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### Publications

÷.	J. K. Stille and M. A. Bedford, <u>J. Polymer</u> Sci., B, $4$ , 329 (1966).
2.	J. K. Stille and F. W. Harris, J. Polymer Sci., B, $\frac{4}{2}$ , 333 (1966).
3.	J. K. Stille, F. W. Harris and M. A. Bedford, <u>J</u> . <u>Heterocyclic</u> <u>Chem., 3</u> , 155 (1966).
4.	J. K. Stille and L. D. Gotter, <u>J. Polymer Sci.</u> , B, <u>6</u> , 11 (1968).
5.	J. K. Stille and M. A. Bedford, J. Polymer Sci., A, 6, 2331 (1968).
6.	J. K. Stille and F. W. Harris, <u>J. Polymer Sci</u> ., A, 6, 2317 (1968).

### Presentations

- J. K. Stille, M. A. Bedford, F. W. Harris and L. D. Gotter, "1,3-Dipole Addition Polymers", Presented at the 1.U.P.A.C. Symposium on Macromolecular Chemistry at Brussels-Louvain, 12-16 June 1967.
- M. A. Bedford and J. K. Stille, "Polymers from 1,3-Dipole Addition Reactions - The Sydnone Dipole", Polymer Preprints, American Chemical Society, Division of Polymer Chemistry, Presented at the San Francisco meeting, April 1-5, 1968.

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### ABSTRACT

Methods were sought for the synthesis of thermally stable, oil resistant elastomers based on chains containing aromatic heterocyclic rings. Three 1,3-dipole precursors, the sydnone, the hydrazide chloride, and the tetrazole systems were studied in terms of their usefulness as monomers for 1,3-dipolar addition reactions. Of the three, only the tetrazoles show promise as useful monomers. A series of polymers which possessed moderate viscosities, high thermal stabilities, and high polarity was generated via the 1,3-dipolar addition reaction. In general, the polymers showed high second-order transition temperatures and efforts to decrease the transition temperature by incorporating flexible linkages into the polymer were unsuccessful. Methods of synthesis and characterization of monomers, model compounds, and polymers are described.

### INTRODUCTION

Cycloaddition reactions can be employed in theory as a mode of propagation in the synthesis of macromolecules; the 1,2-, 1,3-, and 1,4-cycloadditions are well known organic reactions. The Diels-Alder reaction has been used as a means of synthesizing polymers.<sup>1</sup> Although the reaction has been employed to prepare a variety of polymers containing rings in the backbone, it seldom yields high molecular weight polymers because of the frequency of side reactions and the ease with which the reverse reaction takes place. 1,2-Addition reactions aren't particularly good as polymerization reactions since the yields are usually too low to be effective propagation modes, and the additions must be either photocatalyzed,  $^2$  or, if they are thermally induced,  $^3$ the olefins must be substituted with groups which would make monomer synthesis very difficult. In addition, the strain that exists in cyclobutane rings makes polymeric systems containing such rings susceptable to degradation; the reverse cycloaddition occurs readily at elevated temperatures.



Many of the 1,3-dipole addition reactions<sup>4</sup> are suitable for use as polymer forming reactions since the difunctional monomers can be synthesized readily and many of the dipolar reactions are nearly quantitative. Especially suited to the production of stable polymers is the fact that certain products of the 1,3-dipolar addition reactions are five-membered aromatic heterocycles. Thus, when the dipolarophile is a triple bonded species such as an acetylene or a nitrile and the dipole contains an atom, Y, which possesses a lone pair of electrons in the product, the ring contains the requisite 6- $\mathcal{T}$  electrons.

The object of this study was to obtain elastomeric, oil resistant, thermally stable polymers. Through recent advances in the area of heat stable polymers<sup>5</sup> it became clear that if an organic polymer was to achieve a high degree of thermal

stability, it would have to contain only non-degradable structures such as aromatic or pseudoaromatic units, perfluoro units, etc. In order to make the polymer elastomeric and oil resistant, the polymer must have a reasonable number of highly flexible units to maintain its flexible propertier, and a large number of highly polar groups in order to impart oil resistance to the majority of nonpolar lubricants. Systems containing pyrazole and triazole units appeared to be desirable in terms of polarity and aromaticity. These units are obtainable through the 1,3-dipolar addition reactions of sydnones and nitrilimines with acetylenes or nitriles. In this report we outline the synthesis and polymerization reactions of bissydnone and bisnitrilimine dipoles with double dipolarophiles. 

### DISCUSSION

Sydnones are generally prepared by the dehydration of N-nitroso- $\alpha$ -amino acids.<sup>6,7</sup> The addition of acetylenes to sydnones produces pyrazoles and the reaction is facilitated by the presence of polar groups attached to the acetylene.<sup>8,9</sup> The reaction presumably goes through an intermediate Diels-Alder type adduct with subsequent loss of carbon dioxide. The cycloadditions afford predominately one isomer when the possibility of several isomers exist and the direction of

addition usually can be predicted from a consideration of sites in both the dipole and dipolarophile.



Nitrilimines may be generated by the action of base on acid hydrazide chlorides or by the thermal decomposition of tetrazoles.<sup>9-14</sup> Nitrilimines react rapidly with alkynes and alkenes to form pyrazoles and pyrazolines, respectively.<sup>10</sup> Although the dipolarophile activity of the nitrile group is less, triazoles are formed when the nitrilimine dipole is generated in the presence of nitriles.<sup>12</sup> Also only one



pyrazole or triazole isomer has been reported when two are possible and the yield of pyrazole or triazole is increased by the presence of electron withdrawing groups attached to the dipolarophile.

### Monomers

Several bissydnones have been synthesized. Both monomers  $(1a)^{15,16}$  and  $(1b)^{17,18}$  have been synthesized from hexamethylenediamine and p-phenylenediamine starting materials, respectively, by conventional amino acid syntheses, followed by the sydnone forming reactions.





The bromination of 3-phenylsydnone to form 4-bromo-3phenylsydnone and the treatment of this intermediate with several reagents to give bissydnone products have been reported.<sup>19</sup> The reaction of the brominated sydnone with thiourea afforded the di-4-(3-phenylsydnone)sulfide (2a).<sup>20</sup> 4-Lithiosydnone (3) could be formed from the reaction of the bromosydnone with butyllithium or from the direct lithiation of 3-phenylsydnone with butyllithium.<sup>21</sup> The reaction of the lithio derivative with phosgene, yielded the di-4-(3-phenylsydnone)ketone (2b).<sup>20,22</sup> The disydnone, 4,4'-bis(3-phenylsydnonyl)sulfoxide (2c),<sup>23</sup> was also prepared from the lithium salt. 4,4'-Mercuri-bis-3-phenylsydnone (2d) was prepared according to the described method.<sup>20,24</sup>









2 g

2 h

Since it was possible that electron-withdrawing groups such as the carbonyl groups on the sydnone ring might affect the 1,3-dipolar addition, an attempt was made to prepare a similar bissydnone without these groups. Unfortunately, the reaction of the lithium salt of 3-phenylsydnone with 1,4dibromobutane did not give the expected product (4).<sup>25</sup>

The synthesis of 3-phenylsydnone-4-carboxylic acid (5)was effected by the direct lithiation of 3-phenylsydnone and the subsequent carbonation of this intermediate according to the known procedure.<sup>21,23</sup> This acid was converted to 3-phenylsydnone-4-carbonyl chloride (6) as described.<sup>23,26</sup> From this derivative a series of bissydnones was prepared through the reactions of the acid chloride with diamines and diols. Reaction of the acid chloride (6) with 1,6-hexanediamine, <u>m</u>-phenylenediamine, <u>p,p</u>'-methylenedianiline, and hydroquinone gave the respective bissydnones: N,N'-hexamethylene-bis(3phenylsydnone-4-carboxamide) (2e), N,N'-<u>m</u>-phenylenemethanebis(3-phenylsydnone-4-carboxamide) (2g), and p-phenylene-bis(3phenylsydnone-4-carboxamide) (2g), and p-phenylene-bis(3-

Due to the appearance of drug refractory malaria in Southeast Asia, the U.S. Army Medical Research and Development Command

requested that any new compounds that might be effective against malaria be screened by Walter Reed Army Medical Center.

There are some reports which indicate antimalarial activity for sydnones.<sup>27,28</sup> Because of this potential antimalarial activity of sydnones, the series of new sydnones, N,N'-hexamethylenebissydnone (1a), 4,4'-bis(3-phenylsydnonyl)sulfoxide (2c), 4,4'mercuri-bis-3-phenylsydnone (2d), N,N'-hexamethylene-bis(3-phenylsydnone-4-carboxamide) (2e), N,N'-m-phenylene-bis(3-phenylsydnone-4-carboxamide) (2f), N,N'-p-diphenylenemethane-bis(3-phenylsydnone-4-carboxamide) (2g), and p-phenylene-bis(3-phenylsydnone-4-carboxamide) (2g), was submitted for testing. None of the sydnones submitted showed any significant antimalarial activity.

The acid hydrazide chlorides, isophthaloylphenylhydrazide chloride (7a), terephthaloylphenylhydrazide chloride (7b), and 4,4'-oxdibenzoylphenylhydrazide chloride (7c), were prepared by the reaction of phosphorous pentachloride on the respective dihydrazides.<sup>29</sup>

 $C_{6}H_{5}NHNHCArCNHNHC_{6}H_{5} \longrightarrow C_{6}H_{5}NHN=CAT-C=NNHC_{6}H_{5}$ 7. At = 0. m-C<sub>6</sub>H<sub>4</sub> b. p-C<sub>6</sub>H<sub>4</sub> c O - 0 - O These acid hydrazide chlorides eliminate hydrogen chloride on treatment with base to afford the intermediate bisnitrilimine dipole.

7 
$$\xrightarrow{\text{Et}_3 \text{N}}$$
  $c_6\text{H}_5\overline{\text{N}}\text{-N}=\overset{+}{\text{C}}-\text{Ar}-\overset{+}{\text{C}}=\text{N}-\overline{\text{N}}-c_6\text{H}_5$ 

The tetrazoles, 2,2'-diphenyl-5,5'-m-phenyleneditetrazole (8a) and 2,2'-diphenyl-5,5'-p-phenyleneditetrazole (8b), were prepared by the base-catalyzed condensation (sodium in 2-methoxyethanol) of iso- and terephthaloylphenylhydrazone with phenyl azide.<sup>3,3,31,32</sup>

$$C_{6}H_{5}NHN = C - Ar - C = NNHC_{6}H_{5} \longrightarrow N = N$$

8 Ar = 0.  $m - C_6 H_4$ b.  $p - C_6 H_4$ 

When these tetrazoles are heated, they loose nitrogen to yield the same intermediate bisnitrilimine dipoles as the isoand terephthaloylphenylhydrazide chlorides do. The higher

8  $\longrightarrow$   $c_6H_5\bar{N}-N=\bar{c}-Ar-\bar{c}=N-\bar{N}-c_6H_5$ 

reaction temperature and loss of nitrogen instead of hydrogen chloride in this reaction made it an attractive route to the bisnitrilimine dipole.

The diacetylenes <u>m</u>- and <u>p</u>-diethynylbenzene  $(9a,b)^{18,33}$  and the dinitriles, perfluoroglutaronitrile  $(10)^{34,35}$  and 4,4'dicyanobiphenyl (11), were synthesized for use as double dipolarophile monomers.



### Model Compounds

A series of model compounds was synthesized by the reaction of the sydnone and nitrilimine dipoles with acetylene and nitriles. The reactions of 3-phenylsydnone<sup>36</sup> with <u>m</u>- and <u>p</u>-diethynylbenzene, and <u>p</u>-phenylene-3,3'-disydnone (<u>1b</u>) with phenylacetylene, respectively, afforded 1,1'-diphenyl-3,3'-<u>m</u>-phenylenedipyrazole (<u>12a</u>),<sup>34</sup> 1,1'-diphenyl-3,3'-<u>p</u>-phenylenedipyrazole (<u>12b</u>),<sup>29</sup> and 3,3'-diphenyl-1,1'-<u>p</u>-phenylenedipyrazole (<u>13</u>) (Table 1).<sup>18</sup> A study of reaction solvents for these reactions as evaluated both by the evolution of carbon dioxide and the yield of dipyrazole, showed that nitrobenzene and xylene gave higher yields of product than diglyme, while <u>m</u>-dichlorobenzene gave an oil.<sup>29,37</sup> The analogous reaction of (<u>1a</u>) with phenyl-







acetylene was carried out to yield 3,3'-diphenyl-1,l'-hexamethylenedipyrazole (14) in a low (37%) yield.<sup>38</sup>



The reaction of <u>m</u>-divinylbenzene with 3-phenylsydnone in refluxing xylene afforded a 95% yield of 1,1'-diphenyl-3,3'-<u>m</u>-phenylene- $\Delta^2$ -pyrazoline (15).<sup>23</sup>



The compound 2,4,6,8-tetrahydro-4,8-dioxo-2,6-diphenylpyrazolo- $\overline{/3},4-\underline{f}/$ indazole (16) was prepared by the reaction of 3-phenylsydnone with p-benzoquinone.<sup>31</sup> A much higher yield than that reported<sup>39</sup> was obtained by the use of nitrobenzene as the reaction solvent. An oxidation takes place since the loss of four atoms of hydrogen is required, and nitrobenzene or quinone may serve as the oxidizing agent. If nitrobenzene is used, then the stoichiometry for the reaction would be a simple 2:1 molar balance as illustrated:



However when nitrobenzene is not present then the stoichiometry for the reaction would be a 2:3 ratio as shown:



If the reaction were run in air, then air oxidation could take place to reoxidize the hydroquinone back to quinone and the above statements might not be entirely valid. Nevertheless, since most polymerizations are run in an inert atmosphere such as nitrogen, a polymerization of this type could not take place unless the above monomer balance was followed.

Reactions of the sydnones (2a-2h) with phenylacetylene were investigated.<sup>25</sup> Although the same conditions were employed as those used in the reactions of 3-phenylsydnone and p-phenylene-3,3'-disydnone with phenylacetylene, (with the exception of (2d) which produced free mercury) only starting compound was recovered and no evolution of carbon dioxide was noticed. It appears that the electronic effect of the different groups such as carbonyl, sulfur, or amido might have hindered the 1,3-dipolar addition. With the mercury compound, it is quite probable that decomposition of the bissydnone took place before any addition reaction. The reactions of the acid hydrazide chlorides (7a, b) with phenylacetylene, and the reactions of <u>m</u>- and <u>p</u>-diethynylbenzene (9a,b) with benzoylphenylhydrazide chloride in the presence of base were carried out.<sup>37</sup> These reactions afford 1,1',5,5'-tetraphenyl-3,3'-<u>m</u>- and <u>p</u>-phenylenedipyrazole and 1,1',3,3'-tetraphenyl-5,5'-<u>m</u>and <u>p</u>-phenylenedipyrazole, respectively.<sup>29,40</sup> In addition, the analogous reactions of (7c) with phenylacetylene and benzoylphenylhydrazide chloride with (10) and <u>m</u>-divinylbenzene were carried out to afford a series of model compounds (Table 2).<sup>20,34,41</sup>





TABLE 2 MODEL COMPOUNDS FROM ACID HYDRAZIDE CHLORIDES

10.82 10.66 10.87 3.10 13.93 10.71 10.71 9.18  $Z_i$ 5.26 5.99 5.01 5.25 5.27 5.02 FOUND 비 83.73 62.75 84.34 83.98 84.12 82.76 83.37 Ч ANALYSIS 10.89 10.89 10.89 10.89 10.80 14.23 9.23 꾀 CALC'D 5.09 5.09 5.09 5.09 5.83 3.41 4.94 피 63.05 84.01 84.01 84.01 83.14 84.01 83.37 Q ပါ 236-238 247-248 210-211 197-198 269-271 212-214 211-213 M.P. e e зо Бо л До r v 65 − N 64 يد 1 لارولو £ Cet 2 COMPOUND MODEL C F2)34 -N<sup>EH5</sup> N - N SH3 `cH 65∕⊾ цр Тр GH 65 S. S. ာ မီ (F) SH сно Но л З о Чо С CH=CH DIPOLAROPHILE C<sub>6</sub>H<sub>5</sub>C≡CH c H-c≡cH с<sub>6</sub>н₅с≡сн 9a g 10 CHIICH 7a dĽ 70 Cette CHIN-N FDRAZIDE ILORIDE ACID ច Ч То Although a number of the model compounds from tetrazoles were expected to be identical to those obtained from the corresponding hydrazide chlorides, the model reactions were carried out for the tetrazoles because of the more stringent conditions required for generation of the nitrilimines from tetrazoles. The reactions of 2,5-diphenyltetrazole and 2,2'-diphenyl-5,5'p-phenyleneditetrazole (8b) with phenylacetylene and benzonitrile were carried out.<sup>25,31</sup> The analogous reactions of 2,5-diphenyltetrazole with <u>m</u>- and <u>p</u>-diethynylbenzene (9a,b) and with terephthalonitrile yielded the expected model compounds (Table 3).<sup>31</sup> Although 2,2',3,3'-tetraphenyl-5,5'-p-phenyleneditriazole was obtained in good yield from the reaction of 2,2'-diphenyl-5,5'-p-phenyleneditetrazole (8b) with benzonitrile, no product has ever been isolated from the reaction of 2,2'-diphenyl-5,5'-m-phenyleneditetrazole (8a) with benzonitrile.

### Polymers

The polymerization reactions of the sydnones with the diacetylenes afforded polypyrazoles in variable conversions. The reactions with p-phenylene-3,3'-disydnone (1b) and the diacetylenes gave nearly quantitative yields of polypyrazoles.<sup>34,40</sup> However, the reactions with N,N'-hexamethylene-disydnone and the diacetylenes afforded the polymer in low yields.<sup>16</sup> This is not

AZOLE AZOLE DIPOLJ	T MODEL COMPOUN MODEL	L ND <u>M.P. <sup>O</sup>C</u> .
SC≡N Cetts COMPOUND I L	2	. ос.
AROPHILE MODEL MODEL COMPOUND M.P. <sup>O</sup> C. C <b>Cells</b> Compound M.P. <sup>O</sup> C. C <b>Cells</b> 102-4 80.8		O}
AROPHILE MODEL CALC'E CALC'E CALC'E CALC'E CALC'E CALC'E E CALC'E E E COMPOUND M.P. <sup>O</sup> C. ⊆ H E E E E E E E E E E E E E E E E E E	CALC'D	C HIC,D
AROPHILE MODEL CALC'D	CALC'D	CALC'D ANAL
APPHILE MODEL AROPHILE COMPOUND M.P. $O_{C}$ , $C$ $H$ $M$ $C$ $c \in H$ $M$ $M$ $C$ $c \in H$ $M$	calc'D	CALC'D C H N C

unexpected considering the low yield of (14) obtained from the reaction of (1a) with phenylacetylene. Polymers (17a,b) whose spectra were nearly superimposable to those of the corresponding model compounds, were obtained when the reactions were carried out in nitrobenzene at  $190^{\circ}$ C. Polymers (18a,b) whose spectra were also very similar to those of the corresponding model compound, were prepared in tetralin at  $175^{\circ}$ C. These polymers



were slightly soluble in such polar solvents as dimethylformamide, dimethylacetamide, and hexamethylphosphoramide. Only low molecular weight polymers were obtained (Table 4). The low molecular weights could be due to precipitation of the polymer before it reached a high molecular weight, but when the reaction was carried out in a sealed tube at 250°C under such conditions that the polymer did not precipitate, no increase in molecular weight was noticed.









TABLE 4

-

POLYMERS FROM SYDNONES

		2	19.14	17.99	18.96	18.82	18.60			
	FOUND	비	4.34	4.33	6.60	6.42	4.96	1.83	4.93	
SIS		이	74.12	75.97	74.05	73.50	75.21	62.54	63.63	
ANAL		21	19.71	19.71	19.16	19.16	19.43			
	CALC'D	비	4.28	4.28	6.90	96.90	5.59 2	2.29	5.22	
ı.	¢	JI JI	76.04	76.04	73.95	73.95	74.97	64.12	62.22	
	a (Air), <sup>C</sup>	;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;	430	400	350	390	410	410	300	
	آير آ	 _	0.35ª	0.40ª	q01′0	0.40 <sup>b</sup>	0.11 <sup>b</sup>	0.60 <sup>b</sup>	0.12 <sup>b</sup>	
. VNC	)) )) %		06	06	30	45	50	63	50	
хмев	гоа		17a	17b	18a	18b	19	20	21	

- Inherent viscosities were obtained in hexamethylphosphoramide at a concentration of 0.25 g./100 ml. . თ
- Inherent viscosities were obtained in tetrafluorodichloroacetone at a concentration of 0.25 g./100 ml. . Д
- The polymers exhibited no significant difference in thermal stability in nitrogen atmosphere. ю о

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FIGURE 1



The polymerization of (1b) with <u>m</u>-divinylbenzene in nitrobenzene gave polymer (19) containing the pyrazoline unit.<sup>41</sup> The spectra of the model compound (15) and the polymer were nearly superimposeable.

The polymerization of (1b) with p-benzoquinone in nitrobenzene at 190°C gave a 63% yield of poly/2, 4, 6, 8-tetrahydro-4, 8-dioxo-2, 6-p-phenylpyrazolo/3, 4-f/indazole/ (20).<sup>41</sup> Unlike the polymers (17a,b), polymer (20) remained in solution. An inherent viscosity of 0.6 was obtained for this polymer (Table 4). The polymerization of N,N'-hexamethylene-bis-sydnone and p-benzoquinone was carried out to yield poly/2, 4, 6, 8-tetrahydro-4, 8-dioxo-2, 6-hexamethylenepyrazolo/3, 4-f/indazole/ (21)<sup>38</sup> in a 40% yield. An inherent viscosity of 0.12 was obtained (Table 4). The infrared spectra of polymers (20) and (21) showed the characteristic maxima displayed by the corresponding model compound (16).

Thermogravimetric analyses (Table 4, Figure 1) of the polymers (17a,b), (19), and (20) showed breaks near  $420^{\circ}$ C in air and  $500^{\circ}$ C in nitrogen. Polymers (18a,b) and (21) showed breaks near  $400^{\circ}$ C in air and  $420^{\circ}$ C in nitrogen.

X-Ray powder patterns showed the polypyrazoles (17a,b)and (18b) to be highly crystalline; however, polymer (18a)showed very little crystallinity. Differential thermal analyses of the polymers shows (18b) having a crystalline transition temperature at 155°. Polymers (17a,b) and (18a) show no crystalline transition; presumably these lie above the decomposition temperature. Second order transition temperatures were found for (17a) (75 and 80°c), (17b) (75 and 100°c), (18a) (70°c) and (18b) (55 and 80°c). Polymers containing the  $(CH_2)$  link show slightly lower second order transition temperatures; polymers containing the p-phenylene link display two second order transitions.

In the nitrilimine dipole system, the reactions of the acid hydrazide chloride monomers (7a-c) with the diynes (9a,b) in refluxing anhydrous tetrahydrofuran in the presence of triethylamine afforded the polypyrazoles (22-24) in high conversions (Table 5).<sup>34,40</sup> Similarly, the polypyrazoline (25) was obtained when an olefin dipolarophile, <u>m</u>-divinylbenzene, was employed in the polymerization reaction with terephthaloyl-phenylhydrazide chloride (7b).<sup>41</sup>



The polymerization of (7b) with perfluoroglutaronitrile (10) in a sealed tube in anhydrous tetrahydrofuran and in the presence of triethylamine afforded the polytriazole (26) containing perfluoromethylene units in the chain.<sup>20</sup> Although

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POLYMERS FROM ACID HYDRAZIDE CHLORIDES

TABLE 5

													/100 ml.
		2	13.04	14.55	12.33	10.54	9.98	12.63	15.86	13.98	16.09	16.63	f 0.25 g./
		FOUND <u>H</u>	4.37	4.50	4.38	4.79	5.13	5.54	3.53	3.99	5.21	6.38	itration o
OKIDES	SISI	U)	80.85	80.46	80.95	81.00	80.45	81.00	59.70	66.34	75.17	74.40	t a concer
	ANAL	뵈	12.83	12.83	12.83	12.83	10.60	12.72	16.40	14.50	18.05	18.05	nic acid a
			4.62	4.62	4.62	4.62	4.58	5.49	2.75	3.65	4.55	4.55	n 98% for
	ېم	0  _	82,55	82.55	82.55	82.55	81.80	81.79	58.60	65.26	77.40	77.40	obtained i
	12:2) 85		500	500	500	500	460	360 <sup>°</sup>	350	275	300	310	es were
	- 10	2	0.11	0.10	0.14	0.32	0.15	0.28	0.13	0.10	0.08	0.26	viscositi
۰۵	CON	%	85	80	82	68 8	78	16	75	77	16	94	Inherent
ਬਤ	WAT	ЬС	22æ	22b	23a	23b	24	25	26	27	28a	28b	ы. Т

See Fig. 2.

ö

. д

The polymers exhibited no significant difference in thermal stability in nitrogen atmospheres.



the reactions of acid hydrazide chlorides with alkyl nitriles in the presence of triethylamine generally do not give high yields of triazoles, electron withdrawing groups attached to the cyano function have been shown to increase the yield dramatically.<sup>12</sup>

Since carbon disulfide has been reported to undergo cycloaddition reactions with 1,3-dipoles, $^{40}$  a polymerization employing this dipolarophile was carried out. The reaction of (lb) with carbon disulfide in tetrahydrofuran in the presence of triethylamine gave the polymer (27) containing spiro-bisthiadiazole units. $^{20}$ 

The infrared spectrum of each polymer sample showed maxima characteristic of the particular heterocyclic structure which it possessed and could be compared directly to the spectrum of the corresponding model compound.









All of the polypyrazoles from hydrazide chlorides were completely soluble in 98% formic acid. The solubility of (22a), for example, which contains all <u>m</u>-phenylene links along the chain is much greater in polar organic solvents (hexamethylphosphoramide) than (23b), which contains all <u>p</u>-phenylene links.

The high thermal stabilities of the polypyrazoles in both air and nitrogen atmospheres are comparable with those of other polymers containing heterocyclic aromatic rings in the backbone. A comparison of the thermogravimetric analysis of the polypyrazoline (25) with the polypyrazoles (22-24) is particularly interesting. An initial break in the curve in air (Fig. 2) is obtained at  $360^{\circ}$ C and, after approximately a 15% weight loss the remainder of the curve follows that of the polypyrazoles and shows a break at  $520^{\circ}$ C. In nitrogen, the thermogravimetric analysis of the polypyrazoline shows a break followed by complete decomposition at  $360^{\circ}$ C. This greater ultimate stability in air rather than nitrogen can be explained on the basis of the oxidation or dehydrogenation of the pyrazoline moieties to pyrazole units.<sup>43</sup> The 15% weight loss is of course greater than



that calculated for the loss of hydrogen only, so evidently some pyrazoline groups are degrading before their oxidation takes place. The infrared spectrum indicates that this preliminary degradation proceeds with the incorporation of nitrile groups  $(2220 \text{ cm}^{-1})$  into the polymer backbone. This conversion of pyrazoline to pyrazole was supported by comparing the infrared spectrum of the polymer taken just following the  $360^{\circ}$ C break,

but prior to the 520°C break, to the spectra of the untreated polypyrazoline and corresponding polypyrazole.

A possible reason for the relatively low viscosities obtained for the polymers derived from nitrilimines is that . side reaction during polymerization may be occurring to upset the monomer balance. Nitrilimines are known to undergo head-to-tail self-dimerization reactions in the absence of a good dipolarophile.44 In fact, dihydrotetrazine polymers (28a,b) can be obtained from the reactions of iso- and terephthaloylhydrazide chloride with triethylamine in refluxing tetrahydrofuran.<sup>16,40</sup> This reaction could, in fact, account for the rather low molecular weights (inherent viscosities, Tables 5 and 6) of the polymers obtained in the cycloaddition reaction of the nitrilimines. Thus a disruption of monomer balance through the self-dimerization would afford low molecular weight polymers with acetylene or nitrile ends. This dimerization could also explain the difficulty encountered in obtaining good elemental analyses on the polymer samples (Tables 5 and 6). Altering the initial monomer balance over a range of larger molar ratios of acid hydrazide chloride and tetrazole to dipolarophile, however, did not increase the molecular weight. All polymers were obtained in high yields.



In the case of the acid hydrazide chlorides, most of the polymerization reactions were carried out near room temperature in the presence of base, however, in the case of the tetrazoles, because of the higher reaction temperatures  $(160-220^{\circ}C)$ ,  $^{11}$ ,  $^{45}$  all of the polymerizations were carried out inside of evacuated sealed reaction tubes.

The reaction of tetrazoles (8a,b) with <u>m</u>- and <u>p</u>-diethynylbenzene (9a,b) in tetralin or 1,2,4-trichlorobenzene solvent afforded the polypyrazoles (22-23) in high yields (Table 6).<sup>25,32</sup> Although the nitrilimine dipoles from acid hydrazide chlorides did not react to any great extent with nitriles, with the exception of (10), the nitrilimine dipoles from the tetrazoles (8a,b) did react to produce a series of polytriazoles (29-32) in good yield. Possibly the higher reaction temperature obtain-



22 a. m-C<sub>6</sub>H<sub>4</sub> b. p-C<sub>6</sub>H<sub>4</sub>



able with the tetrazoles produced more reactive nitrilimine dipoles. The reactions of tetrazoles (8a,b) with perfluoroglutarylnitrile (10), <sup>20</sup> terephthalonitrile, <sup>38</sup> tetrafluoroterephthalonitrile<sup>32</sup> and 4,4-dicyanobiphenyl  $(11)^{23}$  yielded a series of polytriazoles having viscosities ranging to 0.4 (Table 6).





b. p-CgH4

TABLE 6

POLYMERS FROM TETRAZOLES

		2	9.96	10.77	11.05	11,15					15.51	15.35	15.49	15.27	
	FOUND	비	5.26	4.90	5.14	5.19	3.44	2.78	98 98 98	4.09	2.72	2.96	4.31	4.11	
SIS		U V	85.07	82.05	83.22	82.94	58.46	58.67	75.61	77.10	67.24	68.33	78.78	77.29	
ANĀLN		2	12.84	12.84	12.84	12.84	16.40	16.40	19.18	19.18	16.47	16.47	16.34	16.34	
		H	4.59	4.59	4.59	4.59	2.74	2.74	4.11	4.11	2.75	2.75	4.28	4.28	
	יט	୦ 	82.57	82.57	92.57	82.57	58.60	58.60	76.71	76.71	65.88	65.88	80.00	80.00	
	GA (Air),	.00 0	470	500	470	450	370	460	450	430	470	470	450	440	
	۹ ا	 	0.35ª	1.03 <sup>a</sup>	0.41 <sup>a</sup>	1.67 <sup>a</sup>	0.10 <sup>b</sup>	0.18 <sup>b</sup>	0.16 <sup>b</sup>	0.11 <sup>b</sup>	$0.14^{b}$	0.400	0.15 <sup>b</sup>	0.05 <sup>b</sup>	
'ANO	S %	,   	92	16	92	89	94	89	80	65	16	81	70	80	
XMER.	104		22a	22b	23a	23b	29a	29b	30a	305	31a	31b	32 <b>a</b>	32'n	e F

- Intrinsic viscosities were obtained in 98% formic acid at a concentration of 0.30 g/100 ml. Intrinsic viscosities were obtained in 1,2,4-trichlorobenzene at a concentration of 0.30 g/100 ml. . ທຸດ
  - ບ່າບໍ່

Intrinsic viscosities were obtained in nitrobenzene at a concentration of 0.30 g/100 ml. The polymers exhibited no significant difference in thermal stability in nitrogen atmospheres (Fig. 3).





FIGURE 3

Although problems of polypyrazole solubility were encountered especially when tetralin was used as a solvent, samples of all of the polypyrazoles were eventually obtained which had the viscosities indicated (Table 6), and which were completely soluble in 98% formic acid. Treatment of the tetralin to remove peroxides, resulted in polymers having higher viscosity and solubility, thus the insoluble samples probably contained a high degree of crosslinking due to the presence of peroxides during the polymerization reaction. The polypyrazoles from tetrazoles were similar to those obtained from hydrazide chlorides in that the solubility increased and viscosity lowered as the percentage of <u>m</u>-phenylene linkages was increased. Most of the polytriazoles were insoluble in 98% formic acid, but were soluble in 1,2,4trichlorobenzene.

The thermal stabilities of the polypyrazoles (22-23) derived from tetrazoles were comparable to the stability of the corresponding polymer derived from hydrazide chlorides. In general, the polytriazoles seemed to be about as stable as the polypyrazoles. Each underwent only partial decomposition when heated under nitrogen to  $800^{\circ}$ C. (Fig. 3). This probably accounts for some of the difficulty in obtaining satisfactory values for elemental analysis on the polymers. This was especially not: ceable in the

case of the triazole polymers where definite tailing of the  $CO_2$ peaks could be detected on the F and M Model 185 Carbon, Hydrogen, Nitrogen Analyzer (Table 6).

Differential thermal analyses of the polymers derived from tetrazoles showed second order transitions for (22-23) at 240-255°C. with the transition temperature increasing as the number of <u>para-linkages</u> increased. Second order transitions were also found for the polytriazoles (29-32) (Table 7).

### TABLE 7

#### SECOND ORDER TRANSITION TEMPERATURES

Polymer

#### Transition Temperature

22a	240
22b	250
23a	245
23b	255
29a	130, 340 <sup>a</sup>
29b	250, 365 <sup>a</sup>
30a	200, 300 <sup>a</sup>
30b	225, 320 <sup>a</sup>
31a	125, 265
31b	225
32a	140, 270
32b	210, 255

a. Polymer appeared to melt at this point.

In the case of the polytriazoles (29-32), the transitions range 25-120°C, higher for the polymer derived from the <u>p</u>-bistetrazole than for the corresponding one derived from the <u>meta-</u> isomer.

### CONCLUSIONS

Of the three types of 1,3-dipole precursors used in this study, only the tetrazole system shows promise of being a useful monomer system for 1,3-dipolar addition polymerizations. Although model compounds were prepared in most cases before polymerizations were carried out, the procedure wasn't completely reliable. Occasionally the polymers weren't comparable to the model compounds in terms of physical properties. In addition, the yield of model compound couldn't be taken as an indication of what to expect in terms of yield of polymer.

In general, the polymers showed good thermal stability. The polymer structures are polar and therefore, should show good oil resistance to must nonpolar lubricants. The polymers are, for the most part, basic in nature and soluble in acids.

Differential thermal analysis of the polymers containing a high percentage of aromatic linkages show second order transitions at temperatures far higher than desired for polymers which would be expected to show elastomeric properties at room temperatures.

Attempts to incorporate flexible units such as the perfluoroglutaryl linkage into the polymer chains in order to lower the

second order transition temperature were unsuccessful due to poor monomer reactivity and difficulty in monomer synthesis.

#### LITERATURE CITED

- 1. J. K. Stille, Fortschr. Hochpolym. Forsch., 3, 48 (1961).
- See for example, N. J. Turo, "Molecular Photochemistry", W. A. Benjamin, Inc., N. Y., 1965, p. 194.
- 3. J. D. Roberts and C. M. Sharts, <u>Organic Reactions</u>, <u>12</u>, 1 (1962).
- 4. R. Huisgen, <u>Angew. Chem.</u>, <u>75</u>, 604 (1963); <u>Int. Ed.</u>, <u>2</u>, 565 (1963); <u>Chem. Weekblat</u>. (Amsterdam), <u>59</u>, <u>89</u> (1963); <u>Dechema</u> <u>Monograph</u>, <u>49</u>, 201 (1964); <u>Bull. Soc. Chim. France</u>, 3431 (1965).
- 5. See for example, "Symposium on Novel Polymer Structures", <u>Polymer Preprints, American Chemical Society, Division of</u> <u>Polymer Chemistry</u>, presented at the New York Meeting, Sept. 1963, Vol. 4, No. 2, p. 1-57. "Symposium on Ring Containing Polymers", <u>Polymer Preprints, American Chemical Society</u>, <u>Division of Polymer Chemistry</u>, presented at the Philadelphia Meeting, April 1964, Vol. 5, No. 1, p. 114-243.
- 6. W. Baker and W. D. Ollis, <u>Quart. Rev.</u> (London), <u>11</u>, 15 (1957).
- 7. R. H. C. Stewart, Chem. Rev., 64, 129 (1964).
- R. Huisgen, R. Grashey, H. Gotthard, and R. Schmidt, <u>Angew</u>. <u>Chem.</u>, <u>74</u>, 29 (1962); <u>Int. Ed.</u>, <u>1</u>, 48 (1962).
- 9. R. Huisgen, Angew. Chem., 75, 742 (1963); Int. Ed., 2, 633 (1963).
- P. Huisgen, M. Seidel, G. Allbillich and H. Knupfer, <u>Tetrahedron</u>. 17, 3 (1962).
- 11. R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, J. Org. Chem., 24, 892 (1959).

- 12. R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, Liebigs Ann. Chem., 653, 105 (1962).
- 13. R. Huisgen, J. S. Clovis, A. Eckell, and R. Sustmann, <u>Chem.</u> Ber., 100, 60 (1967).
- 14. R. Huisgen, H. Knupfer, R. Sustmann, and G. Wallbillich, Chem. Ber., 100, 1580 (1967).
- 15. H. O. Daeniker and J. Druey, <u>Helv. Chim. Acta.</u>, 40, 918 (1957) and patents listed therein.
- 16. Quarterly Progress Report No. 10, 31 July 1967.
- V. G. Yashunskii and L. E. Kholodov, <u>Zh. Obshch. Khim.</u>, <u>32</u>, 3661 (1962); C.A., <u>58</u>, 13939 (1963).
- 18. Quarterly Progress Report No. 1, 30 April 1965.
- 19. H. Kato and M. Ohta, Bull. Chem. Soc., Japan, 32, 282 (1959).
- 20. Quarterly Progress Report No. 7, 31 October 1966.
- C. V. Greco, M. Pesce, and J. Franco, <u>J. Hetero</u>. <u>Chem.</u>, <u>3</u>, 391 (1966).
- N. Suciu, G. H. Mihal, M. Elian and E. Stroescu, <u>Tetra-hedron</u>, 21, 1369 (1965).
- 23. Quarterly Progress Report No. 8, 31 January 1967.
- 24. K. Nakahara and M. Ohta, <u>Nippon Kagaku Zasshi</u>, <u>77</u>, 1306 (1956); Chem. Abstr., <u>53</u>, 5251 (1959).
- 25. Quarterly Progress Report No. 9, 30 April 1967.
- 26. K. Kishimoto and M. Ohta, <u>Nippon Kagaku Zasshi</u>, <u>83</u>, 833 (1962). Chem. Abstr., <u>59</u>, 5152 (1963).
- 27. N. H. Nyberg and C. C. Cheng, J. Medicin. Chem., 8, 531 (1965).
- 28. I. C. Popoff and G. H. Singhal, Abstracts 153 A.C.S., Miami, M20 (1967).

29.	Quarterly Progress Report No. 2, 31 July 1965.
30.	R. Huisgen, M. Seidel, and J. Sauer, <u>Chem. Ber</u> ., <u>94</u> , 2505 (1961)
31.	Quarterly Progress Report No. 6, 31 July 1966.
32.	Quarterly Progress Report No. 12, 31 January 1968.
33.	A. S. Hay, J. Org. Chem., 25, 637 (1960).
34.	Quarterly Progress Report No. 4, 31 January 1966.
35.	C. J. Verbanic, Canadian Patent 685,637 (May 5, 1964).
36.	J. C. Earl and A. W. Mackney, <u>J</u> . <u>Chem</u> . <u>Soc</u> ., 899 (1935).
37.	J. K. Stille, F. W. Harris, and M. A. Bedford, <u>J</u> . <u>Hetero-</u> cyclic Chem., <u>3</u> , 155 (1966).
38.	Quarterly Progress Report No. 11, 31 October 1967.
39.	D. L. Hammich and D. J. Voaden, <u>Chem</u> . <u>Ind</u> . (London) 739 (1956); <u>J. Chem. Soc</u> ., 5871 (1965).
40.	Quarterly Progress Report No. 3, 30 October 1965.
41.	Quarterly Progress Report No. 5, 30 April 1966.
42.	R. Huisgen, R. Grashey, M. Seidel, H. Knupfer and R. Schmidt, <u>Liebigs Ann. Chem</u> ., <u>658</u> , 169 (1962).
43.	I. I. Granberg, W. Ting, A. N. Kostand and V. I. Kozlova, <u>Nhur. Obschei Khim., 31</u> , 544 (1961); <u>ibid.</u> 31, 1892 (1961).
44.	R. Huisgen, E. Aufderhaar, and G. Wallbillich, <u>Chem</u> . <u>Ber</u> ., 98, 1476 (1965).
45.	0. Dimroth and S. Merzbacher, Ber. dtsch. Chem. Ges., 40, 2402 (1907).

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