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Summary of Proposed Research

It was proposed to investigate two novel routes for synthesis of potentially thermally stable polymers. A common type of coreactant in each of these routes is a suitable bis-triazolinedione. The first route involved a novel reaction of bis-triazolinediones with substituted styrenes. The second route involved the reaction of suitable divinyl esters with bis-triazolinediones in a novel intra-molecular 1,4-dipolar rearrangement in the propagation step. The basic chemistry underlying these two routes to polymers had been done prior to the initiation of the present work, predominantly in these laboratories, and the feasibility of polymer formation had already been demonstrated. Representative examples of polymers had been examined from the standpoint of intrinsic viscosity, molecular weight, molecular weight distribution, preliminary thermal stability, abrasive resistance, etc. and these results were indicative that the proposed polymers would possess interesting and potentially useful properties.

Summary of Research Results

Two research papers dealing with the reaction of bis-triazolinediones with divinyl esters have been prepared and submitted to Journal of Polymer Science, Polymer Letters Edition, for publication. One additional manuscript has been prepared but has not been submitted for publication at this time. Copies of these papers are included in the Appendix of this report. In addition, a copy of the Summary Progress Report of March 30, 1977 is included in the Appendix.

Additional results include synthesis, structure studies, analyses, and polymer properties studies on twenty new polymers derived via reaction of two previously synthesized bis-triazolinediones and four new bis-triazolinediones with eight styrenes. A fundamental study of the reaction of triazolinediones with enol esters is also reported. The synthesis of a novel bis-enol ester is reported along with polymerization studies of this enol ester with bis-triazolinediones. This phase of the study included the synthesis, structural determination, analyses and polymer properties determination on novel polymers derived via reaction of three bis-triazolinediones with three bis-enol esters.

Introduction

This report is based upon research results obtained by University of Florida scientific personnel during the period of September 1, 1976 to August 31, 1977 under the sponsorship of the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135 under grant No. NSG-3120.

Objectives of Research:

The objectives of this research program were to synthesize novel and interesting polymers which may have outstanding thermal stability by the following reactions from the indicated or related reactants:
(1) \[ \text{F} \] 
(2) \[ \text{N} \]
(3) \[ \text{N} \]
(4) \[ \text{O} \]
(5) \[ \text{O} \]
(6) \[ \text{O} \]
Background Information:

I. Thermally stable polymers by reaction of bis-triazolinediones with substituted styrenes

Cookson and coworkers [13] have investigated the Diels Alder reactions of triazolinediones and found that PhTD spontaneously reacts with styrene to yield the double Diels Alder adduct (8). Maleic anhydride [2] and ethyl azobisformate [3] have been shown to react with styrene in a Diels Alder fashion, but the final products in both cases were those products which resulted from an ene reaction after the first Diels Alder reactions.

We interpreted Cookson’s results to mean that styrene, potentially, would be an attractive bis diene to investigate with (7) to yield polymers having (10) as repeating unit.

However, when PhTD and styrene were mixed [4] in methylene chloride at room temperature (9) was formed rather than the reported Diels Alder adduct (8).
When styrene and (7) were mixed at room temperature in dimethylformamide, a polymer was formed instantly. The polymer was soluble in both dimethylformamide and dimethylsulfoxide. The thermal decomposition was recorded using a Differential Scanning Calorimeter and was found to start at 307°C. An intrinsic viscosity determined in dimethylformamide having η = 0.12 dl/g, based upon a calibration using a polystyrene standard gave a number average molecular weight of 36,000 and a weight average molecular weight of 120,000 for a molecular weight distribution or polydispersity of 3.34. Structure (10) was assigned to this polymer although it was later shown [5] to consist of only about 67% of these units, the remaining 33% being units of structure (8). It has recently been shown that certain p-substituents, e.g., p-F, promote almost exclusive formation of structure (10) in such copolymers [6]. It is predicted that these homopolymers should be more stable than the copolymers obtained earlier, and that their physical properties should be considerably improved.

One of the problems inherent in such systems for synthesizing high polymers is stoichiometry. Thus, as in step-wise polymerization via condensation reactions, e.g. between a dihydric alcohol and a dibasic acid, exact stoichiometric balance between the two reactants is important in order to attain high molecular weight. In the preliminary work on the substituted styrene systems [6] studies to date because of the limited quantities of the reactants available, no careful studies on exact stoichiometric balance have been attempted and no studies of polymer properties were conducted. The studies to date were predominantly oriented toward determination of the ratios of the repeating units (8) and (10) and to the role of the substituent on controlling this ratio.

Thus, it is proposed to extend this research to include further studies of substituent effects on the styrene molecule, and to the role of the substituent on controlling the ratio of structures (8) and (10), as well as to evaluate the effect of the stoichiometric balance on molecular weight, and to prepare sufficient quantities of representative polymers to permit an evaluation of their properties both from the fundamental and applied standpoints. Efforts would be directed toward obtaining essentially pure homopolymers of both structures (8) and (10) as the result of the substituent effect experiments.

II. Synthesis of thermally stable polymers by reaction of bis-triazoline-diones with divinyl esters in a novel 1,4-dipolar rearrangement

PhTD (11) has been shown to undergo reaction with vinyl ethers to produce alternating 1:1 copolymers via linking of 1,4-dipolar intermediates [7].
The existence of the intermediate 1,4-dipole and its probable participation in the copolymerization process was proven by its reaction with ketones in trapping experiments to yield novel 1,3,4-tetrahydrooxadiazenes [8] as shown in structure (12). Extension of this reaction to vinyl esters was envisioned as a means of producing alternating 1:1 copolymers of these novel structures. However, the major course of the reaction of (11) with vinyl acetate (13) was through the intermediate 1,4-dipole, followed by a novel intramolecular rearrangement to yield new and interesting structures as shown in (14)[9]. The existence of the intermediate dipole and its probable participation in the rearrangement has been supported by kinetic evidence as well [10]. It follows that this novel reaction becomes polymer-forming by making each of the reactants bifunctional as shown in Reaction II above.

Preliminary experiments have been conducted to demonstrate the feasibility of this intramolecular dipolar rearrangement in synthesizing linear polymers [10] as shown in Scheme I. Both low molecular weight linear polymers having spectral and analytical characteristics consistent with the proposed structures, and lightly cross-linked, solvent-swellable gels were obtained in these experiments. However, because of the limited quantities of the reactants available, extensive efforts to obtain stoichiometric balance of co-reactants were not made. Thus, it was proposed to continue these studies to include synthesis of suitably substituted divinyl esters of dibasic acids [11], to
subject these esters to polymer formation via reaction with a suitable bis-
triazolinedione, under conditions of rigidly controlled stoichiometric
balance, and to investigate the fundamental properties of the resulting
polymers. The monomers would be designed to impart to the resulting polymers
the maximum effect on thermal stability and/or whatever applied property
may be desired in the product. The extent to which propagation occurred via the
intramolecular dipolar rearrangement reaction would also be determined in
each-case.

The polymer proposed in the reaction (II) would be predicted to possess
excellent thermal stability as the only aliphatic hydrogens are those on the
methylene group derived from the terminal methylene of the original vinyl
group. Also, these aliphatic hydrogens constitute only a small fraction
of the total repeating unit. Further, the results of the kinetic study
[12] have shown that the undesirable side reactions which occur are minimized
by structural effects which stabilize the intermediate dipole.

The coreactant, bis-(α-phenylvinyl)terephthalate (17), was not a
known compound at the beginning of this research. (The synthesis of divinyl-
terephthalate had been reported in Ref. 16). However, since this coreactant,
based upon known substituent effects on thermal stability, would most likely
produce the ultimate in thermal stability attainable by this reaction sequence,
some attention was given to its synthesis. The following synthetic steps
(I and II) had been shown to be operative for similar but not identical
synthetic goals in the respective references cited:

\[
(I) \quad \begin{array}{c}
\text{HO-} \quad \text{O} \\
\text{C-} \quad \text{O-H} + \quad \text{CH}_2=\text{C} - \quad \text{O-C}_2\text{H}_5 \\
\text{[13a]} \quad \text{Trace} \quad \text{[13b]} \\
& \xrightarrow{\text{H}_3\text{PO}_4} \\
\text{C}_6\text{H}_5 \quad \text{O} \\
\text{C-O-C} = \quad \text{CH}_2 + \quad 2\text{C}_2\text{H}_5\text{OH}
\end{array}
\]

\[
(15) \quad (16) \quad (17)
\]

\[
(II) \quad 2\text{CH}_2=\text{C} - \quad \text{O-C}_1 \quad \text{[14a]} + \quad \text{NaOC-} \\
\text{C-OH} \quad \text{[14b]} \\
\begin{array}{c}
\text{C}_6\text{H}_5 \quad \text{O} \\
\text{C-O-C} \quad \text{=CH}_2 + \quad 2\text{NaCl} + \quad 2\text{CO}_2
\end{array}
\]

\[
(18) \quad (19) \quad (17)
\]
Thus it appears entirely feasible to synthesize a wide variety of polymeric structures at low temperatures by reaction of suitable triazoline-dione derivatives with the readily available alkene and diene structures illustrated above. Furthermore, a large portion of the basic chemistry had already been done, largely in our own laboratories, making it possible to devote a large portion of the effort on this project to synthesis of novel polymer systems and to investigation of their properties.

Experimental Procedures and Results (See also Appendix)

A. Synthesis of polymers via reaction of triazolinediones with styrenes

Tables I to III summarize the polymerization conditions, solvent, analyses, and some of the properties of twenty new polymers obtained from the indicated bis-triazolinediones and substituted styrenes.

B. Synthesis of polymers via reaction of triazolinediones with enol esters.

From previous work performed in our laboratory it was found that N-substituted 1,2,4-triazoline-3,5-diones (20) and unsaturated esters (23) react together forming among other compounds mainly 1,4-dipolar-rearrangement products (22):

\[
\begin{align*}
R_1-N=\bigcirc-C-R_2 & \quad + \quad CH_2=\bigcirc-C-R_3 \\
\text{(20)} & \quad \text{(21)} & \quad \text{(22)} \\
\end{align*}
\]

The other products in the above reaction are formed as a result of intramolecular dipole coupling (23) (intermolecular reaction leading to formation of polymer is also possible) and the ene reaction (24). The latter is only possible when allyl hydrogen atoms are present.

Selectivity towards formation of the rearrangement products for substituted vinyl esters (e.g. isopropenyl acetate) according to previous data was close to 100%. Such high selectivity indicated that synthesis of high molecular polymers based on corresponding bis(triazolinediones) and esters of dibasic acids would be promising.

The use of monomers with thermally stable substituents (e.g. R_1, R_2, R_3 aromatic rings) should lead to formation of polymers with very good thermal properties.

The research was divided into three parts:

1. Synthesis of thermally stable esters of dibasic acids
2. Studies of some model reactions involving 1,4-dipolar rearrangement
3. Synthesis of polymers based on 1,4-dipolar rearrangement reaction and their characterization.
Table 1
Polymerization Conditions, Solvent, Analytical Results, and Properties of Polymers via the Bis-triazolinedione-styrene Reaction

<table>
<thead>
<tr>
<th>Styrene</th>
<th>Solvent</th>
<th>Structure (NMR)</th>
<th>DSC (Exo Max) °</th>
<th>[η]</th>
<th>dl/g (DMF)</th>
<th>GPC (DMF)</th>
<th>Calcd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl</td>
<td>CH₂Cl₂</td>
<td>Diels-Alder-ene 289</td>
<td>0.32</td>
<td>20000 C, 63.38 58.90</td>
<td>H, 4.93 5.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>instantaneous</td>
<td></td>
<td></td>
<td>broad</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,4-Dimethoxy</td>
<td>CH₂Cl₂</td>
<td>Diels-Alder-ene 252</td>
<td>0.14</td>
<td>5000 C, 58.74 55.59</td>
<td>H, 4.20 5.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>instantaneous</td>
<td></td>
<td></td>
<td>narrow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Chloro</td>
<td>CH₂Cl₂</td>
<td>Diels-Alder-ene 283</td>
<td>0.27</td>
<td>1400 C, 57.09 52.50</td>
<td>H, 3.48 3.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>instantaneous</td>
<td></td>
<td></td>
<td>narrow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methyl</td>
<td>CH₂Cl₂</td>
<td>mainly 229 and 278</td>
<td>0.27</td>
<td>20000 C, 61.60 55.00</td>
<td>H, 4.18 4.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 min</td>
<td>Diels-Alder-ene (too viscous)</td>
<td></td>
<td></td>
<td>N, 15.97 13.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Nitro</td>
<td>CH₂Cl₂</td>
<td>insoluble 385</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>instantaneous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GPC - the polymers had significant adsorption on the columns; therefore the highest MW were recorded.
Table 2
Polymerization Conditions, Solvent, Analytical Results, and Properties of Polymers via the Bis-triazolinedione-styrene Reaction

<table>
<thead>
<tr>
<th>Styrene</th>
<th>Solvent</th>
<th>Structure (NMR)</th>
<th>DSC (Exo Max) °C</th>
<th>[n] d1/g (DMF)</th>
<th>GPC* (DMF)</th>
<th>Calcd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl</td>
<td>Et Ac</td>
<td>Diels-Alder-ene</td>
<td>303</td>
<td>0.15</td>
<td>4500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 min</td>
<td></td>
<td></td>
<td></td>
<td>narrow</td>
<td>C 64.73</td>
<td>60.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, 4.56</td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N, 17.43</td>
<td>16.14</td>
<td></td>
</tr>
<tr>
<td>3,4-Dimethoxy (1:2)</td>
<td>Et Ac</td>
<td>2 Diels-Alder or Diels-Alder-ene (not conclusive)</td>
<td>315</td>
<td>0.065</td>
<td>6300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td></td>
<td></td>
<td></td>
<td>narrow</td>
<td>C, 59.26</td>
<td>56.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, 3.70</td>
<td>4.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N, 17.28</td>
<td>13.52</td>
<td></td>
</tr>
<tr>
<td>4-Chloro</td>
<td>Et Ac</td>
<td>Diels-Alder-ene</td>
<td>351</td>
<td>0.12</td>
<td>1600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 min</td>
<td></td>
<td></td>
<td></td>
<td>narrow</td>
<td>C, 57.33</td>
<td>52.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, 2.82</td>
<td>3.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N, 18.24</td>
<td>5.14</td>
<td></td>
</tr>
<tr>
<td>4-Methyl</td>
<td>Et Ac</td>
<td>mainly Diels-Alder-ene</td>
<td>315</td>
<td>0.11</td>
<td>8900</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 min</td>
<td></td>
<td></td>
<td></td>
<td>narrow</td>
<td>C, 62.73</td>
<td>57.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, 3.64</td>
<td>3.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N, 19.09</td>
<td>16.39</td>
<td></td>
</tr>
<tr>
<td>3-Nitro</td>
<td>Et Ac</td>
<td>Diels-Alder-ene</td>
<td>365</td>
<td>0.067</td>
<td>4500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hours</td>
<td></td>
<td></td>
<td></td>
<td>medium</td>
<td>C, 56.05</td>
<td>53.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, 2.76</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N, 20.81</td>
<td>15.34</td>
<td></td>
</tr>
</tbody>
</table>

*GPC - the polymers had significant adsorption on the columns; therefore the highest MW were recorded.
<table>
<thead>
<tr>
<th>Bis-triazolinedione</th>
<th>Subst'd. Styrene</th>
<th>Solvent Temp.</th>
<th>Structure (NMR, IR)</th>
<th>$\Delta$ DSC (Exo Max) $^\circ$C</th>
<th>$[\eta]^{30\circ C}$ d/l/g</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="" alt="Image" /></td>
<td>-CH$_3$</td>
<td>DMF, RT</td>
<td>D.A.-ene</td>
<td>242$^\circ$ d</td>
<td>0.295</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>270$^\circ$ d</td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>m-NO$_2$</td>
<td>DMF, RT</td>
<td>--</td>
<td>270$^\circ$ d</td>
<td>--</td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>p-CH$_3$</td>
<td>DMF, RT</td>
<td>D.A.-ene, 2</td>
<td>237$^\circ$, mp</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.A.-D.A., 1</td>
<td>271$^\circ$, d</td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>p-NO$_2$</td>
<td>DMF, RT</td>
<td>D.A.-ene</td>
<td>238$^\circ$, d</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>DMF, RT</td>
<td>D.A.-Ene - 2</td>
<td>190$^\circ$</td>
<td>0.106</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.A.-D.A.- 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>p-CH$_3$</td>
<td>DMF, RT</td>
<td>D.A.-ene - 2</td>
<td>190$^\circ$, d</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.A.-D.A.- 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>p-Cl</td>
<td>DMF, RT</td>
<td>D.A.-ene - 2</td>
<td>264$^\circ$, d</td>
<td>0.142</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.A.-D.A.- 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Image" /></td>
<td>p-NO$_2$</td>
<td>DMF, RT</td>
<td>D.A.-ene</td>
<td>274$^\circ$, d</td>
<td>0.173</td>
</tr>
<tr>
<td></td>
<td>p-t-Bu</td>
<td>DMF, RT</td>
<td>D.A.-ene</td>
<td>200$^\circ$, d</td>
<td>0.092</td>
</tr>
<tr>
<td></td>
<td>-CH$_3$</td>
<td>DMF, RT</td>
<td>D.A.-ene</td>
<td>249$^\circ$, d</td>
<td>0.156</td>
</tr>
</tbody>
</table>
In the present work several esters of mono and dibasic acids were used:

- Isopropenyl acetate, "Aldrich" reagent, used after distillation, bp = 94-95°C.
- Diisopropenyl adipate was prepared from adipic acid (1 mole) and two-fold excess of isopropenyl acetate in an ester exchange reaction. The mixture was refluxed for 30 hrs with 4 g of mercuric acetate as catalyst. It was then washed with a saturated solution of Na₂CO₃ until no more CO₂ was formed and dried over Na₂SO₄. The fraction boiling at 105-106°C (p = 0.25 mm Hg) was collected. The diester was found to be more than 95% pure by ¹H NMR and more than 98% pure by GC. The yield was equal to 12%.
- α-Acetoxy styrene (benzene methanol, α-methylene, acetate) was synthesized by a transesterification reaction between acetophenone (1 mole) and a three-fold excess of isopropenyl acetate using 4 mmoles of p-toluenesulfonic acid as catalyst. The reaction mixture was refluxed for five days followed by fractional distillation. The ester was collected at 96-97°C (p = 4.5 mm Hg) and was found to be 99% pure by GC and NMR.
- α-Benzoxy styrene (benzene methanol, 2-methylene, benzoate) was synthesized via the reaction between benzoyl chloride (0.1 mole) and acetophenone (0.2 mole) in dry triethylamine (1 mole) at 90°C for 24 hrs. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was then dried and distilled. The residue after distilling of all starting product was washed on alumina column with benzene and was found to be 80% pure (NMR). Distillation of that fraction gave a slightly yellow oil (bp = 130°C at 0.3 mm Hg) which crystallized upon cooling. Two recrystallizations from petroleum ether gave long colorless needles in 2% yield (mp = 39°C).
- Distyryl terephthalate and isophthalate were synthesized in a similar way. However, after washing through an alumina column, the purity of the brown oils was about 70% and further attempts to purify them failed. Both oils were used in reactions with bis(triazolinediones) producing insoluble highly crosslinked gels.
- Esters of triphenyl vinyl alcohol (acetate benzoate, terephthalate) were synthesized from the enol tautomer of the ketone (27) which was formed in 70% yield via the Friedel-Crafts reaction between desyl chloride (25) and benzene (26) as white crystals, Mp = 137°C.

![Chemical structures]

- Triphenylvinyl acetate was formed in 15% yield in reaction of the enol with acetic anhydride and potassium acetate. Two recrystallizations from alcohol gave colorless crystals, Mp = 104°C.

- Triphenyl vinyl benzoate was formed in reaction of an etherate suspension of diphenylmethyl potassium and benzoyl chloride. Two recrystallizations from alcohol gave colorless crystals (Mp = 152°C) in 20% yield.

- Formation of bis(triphenylvinyl)terephthalate required a more selective reaction. Potassium triphenylethenolate was synthesized in very dry diglyme from the corresponding alcohol and potassium amide followed by very careful (high vacuum) removal of ammonia. A diglyme solution of terephthaloyl chloride was slowly added under a N₂ atmosphere to the enolate solution and stirred
Scheme I

\[ R_1 \text{O} \left(\text{CH}_2\right)_n \text{O} R_2 \]

\[ \text{CH}_2=\text{C-OO} \left(\text{CH}_2\right)_4 \text{OCO=CH}_2 \]

\[ \text{Insoluble solid} \]

\[ \text{R}_1 \]

\[ \text{R}_2 \]

\[ \text{C}_6 \text{H}_{12} \]

\[ \text{CH}_3 \]

\[ \text{H} \]

\[ \text{CH}_3 \]

\[ \text{H} \]

\[ \text{C}_6 \text{H}_{12} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{C}_6 \text{H}_{12} \]

\[ \text{H} \]
for 4 hrs. The precipitate was filtered, extracted with CHCl₃ and dried over MgSO₄. The solid, after evaporation of CHCl₃, was recrystallized from CH₂Cl₂ giving white crystals melting at Mp = 258° in 30% yield. NMR and LC showed the diester to be more than 97% pure.

Found: C, 85.35; H, 4.97.

-All triazolinediones were synthesized from the corresponding isocyanates and ethyl carbazate to form semicarbazides. The semicarbazides were cyclized in basic media to the urazoles. The urazoles (1,2,4-triazolidine-3,5-diones) were oxidized to the corresponding triazolinediones.

4'-methyl and 4'-phenyl-1,2,4-triazoline-3,5-diones were used as monofunctional compounds.

Bis(p-1,2,4-triazoline-3,5-dione-4-ylphenyl)methane, 1,5-bis(1,2,4-triazoline-3,5-dione-4-yl)naphthalene, and 4,4'-bis(1,2,4-triazoline-3,5-dione-4-yl)-3,3'-dimethoxy diphenyl were used as difunctional reagents.

The reaction between 4-methyl (28a) and 4-phenyl-1,2,4-triazoline-3,5-diones (28b) and isopropenyl acetate (29) was reinvestigated by NMR and UV techniques in different solvents. The reaction leads to formation of two products:

\[
\text{(28)} \quad R = \text{CH}_3, \quad R' = \text{C}_6\text{H}_5
\]

\[
\text{(29)} \quad \text{CH}_3\text{O} \quad \text{CH}_2\text{C} - \text{OCCH}_3
\]

\[
\text{(30)} \quad \text{R-N} \quad \text{R-N} \quad \text{R-N} \quad \text{R-N}
\]

\[
\text{(31)} \quad \text{R-N} \quad \text{R-N} \quad \text{R-N} \quad \text{R-N}
\]

as the result of the ene reaction (30) and the 1,4-dipolar rearrangement (31). The intra- and/or intermolecular dipole couplings for isopropenyl esters do not occur; however, this reaction is sometimes dominant for unsubstituted vinyl esters.

It was reported previously that selectivity of the dipolar rearrangement reaction was close to 100% for isopropenyl esters.

Using higher concentrations of reagents and following the reaction directly in NMR tubes it was found that the ene reaction cannot be neglected and its contribution varies from 9 to 18% for different solvents and different triazolinediones.

The NMR shifts of the products (30a, 31a) are as follows (CDCl₃ solvent)
The following proportions of ene products and rate constant of rearrangement ($K_R$) and ene ($K_E$) reactions were found for 4-methyl-1,2,4-triazoline-3,5-dione at 35°C.

- **CDCl$_3$:** $K_R = 3.2 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$; $K_E = 5.3 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $E = 15\%$
- **C$_6$D$_6$:** $K_R = 1.2 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$; $K_E = 1.7 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $E = 12\%$
- **CH$_3$NO$_2$:** $K_R = 6.7 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $K_E = 1.8 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $E = 23\%$

The phenyl derivative is about 50% more reactive and its reaction is slightly shifted towards rearrangement.

- **CDCl$_3$:** $K_R = 4.5 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$; $K_E = 5.6 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $E = 11\%$
- **C$_6$D$_6$:** $K_R = 1.8 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$; $K_E = 1.8 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$; $E = 9\%$

Some kinetic measurements were also done by the UV technique. This method however, gives only the possibility to determine the sum of both rate constants because it is based on measurements of decreasing absorption of the triazolinedione ($\lambda = 537$ nm). The following values of rate constants were found ($K = K_R + K_E$): $K = 5.3 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$ (CH$_2$Cl$_2$, 35°C); $K = 1.4 \times 10^{-2} \text{M}^{-1} \text{s}^{-1}$ (C$_6$H$_6$, 24°C); $K = 7.18 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ (CH$_3$C$_2$N, 24°C), $K = 2.0 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ (C$_2$H$_5$OC(O)CH$_3$, 24°C); $K = 2.1 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ (THF), 24°C).

The rate constants of the ene reaction between triazolinediones and isopropenyl esters are close to the rate constants of the other unsubstituted olefins (e.g. reaction between 1-hexene and 4-methyl-1,2,4-triazoline-3,5-dione in benzene at 24°C = $K_E = 1.3 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$). The first ene product reacts further with another molecule of triazolinedione, probably forming the double adduct (32):
This reaction was not studied in detail; however, even though it occurs several times slower than the first ene, it still cannot be neglected. This reaction is responsible for the formation of crosslinked polymer when bis-(triazolinediones) react with diesters.

In order to avoid the ene reaction, an α-substituent without allyl hydrogen atoms should be used. Some substituents stabilizing (lowering the energy) the intermediate dipole (33) should accelerate rate of 1,4-dipolar rearrangement reaction (33).

We have chosen as α-substituent (R') the phenyl group (34) which excludes the ene reaction; this group should accelerate rearrangement and should have good thermal stability.

Unfortunately triazolinedione has such powerful dienophilic properties that in addition to the expected 1,4-dipolar rearrangement, the Diels Alder reaction occurs simultaneously:
Adduct (37) reacts further quite rapidly with another molecule of triazolinedione (28) via two pathways: a second Diels-Alder addition (38) and an ene reaction (39).

The Diels-Alder-ene product (39) however is very unstable and rapidly decomposes to the carbanion ion (40) and after elimination of hydrogen atom to the final product (41):
The carbocation has very strong UV absorption ($\lambda = 460$ nm). Conductivity experiments showed an increase of conductivity which was parallel to the increase of the UV peak at 460 nm and shift of the NMR signal from 2.18 to 2.09 ppm followed by slow decrease to a value higher than that of the starting mixture. The dissociation constant of the product (40) is much higher than that of acetic acid (42). The presence of acetic acid (42) can even be detected by its strong typical odor.

When an excess of triazolinedione was used in such experiments, the contribution of the rearrangement decreased in favor of the expected Diels-Alder adduct. Also in the reaction of bis(triazolinediones) with $\alpha$-acetoxystyrene instead of linear poly- and/or oligomers some insoluble gel was formed indicating formation of higher adducts.

The direction of all of the reactions (rearrangement, double Diels-Alder and Diels-Alder-ene) depends mostly on temperature and solvents. The influence of the triazolinedione structure is of minor effect. When reaction between 4-phenyl-1,2,4-triazoline-3,5-dione and $\alpha$-acetoxystyrene (2:1 ratio) was performed at room temperature in CH$_2$Cl$_2$ solvent, the distribution among products equals to 35:38:39 = 43:14:43 while at -70° 35:38:39 = 28:42:30. The activation energy of the rearrangement process is higher than for the Diels-Alder reaction and by decreasing the temperature the process is directed towards the Diels-Alder adducts. The second step consisting of the next Diels-Alder addition has slightly lower activation energy than the ene reaction. The ene product can be treated as the "thermodynamic product" - leading to formation of the stable aromatic ring.

4-Methyl-1,2,4-triazoline-3,5-dione formed with $\alpha$-acetoxystyrene in CH$_2$Cl$_2$ solvent at room temperature products in ratio 35:38:39 = 50:10:35 and at -70° 35:38:39 = 34:36:30.

When $\alpha$-benzoxystyrene was used all reaction products were also observed but analysis of the spectrum was too difficult to determine exact ratios (instead of the singlet of the acetox group, a broad multiplet of the benzoylox group was present.)

The change of the polarity of the solvent changes also the pathway of the reactions (3-3) and (3-4). For example 4-methyl triazolinedione in C$_6$D$_6$ at room temperature gives the following ratio 35:38:39 = 50:0:50 while in CH$_3$NO$_2$ 35:38:39 = 50:5:45. In benzene the double Diels-Alder product is not formed at all.

Another attempt to have pure rearrangement products was the use of triphenylvinyl esters. Two bulky phenyl groups instead of two hydrogen atoms should decrease the probability of the Diels-Alder reaction. Two esters were used, the acetate and the benzoate. In both cases the reaction occurs at a negligible rate (comparable with decomposition of the triazolinedione).
According to our model studies only isopropenyl esters showed promise for synthesis of relatively high molecular polymers via a reaction with bis-triazolinediones. The influence of solvent, temperature, molar ratio, and additions of terminating agents (monoreactive triazolinediones and esters of monobasic acids) were studied. Several different bis-triazolinediones were used.

1. 4,4'-Bis-(1,2,4-triazoline-3,5-dionyl)-3,3'-dimethoxydiphenyl was reacted with diisopropenyl adipate in methylene dichloride and ethyl acetate as shown in Table IV. The reaction was followed until the typical red color of triazolinedione disappeared. In methylene dichloride solution the lowest

<table>
<thead>
<tr>
<th>Exp</th>
<th>bis-TAD</th>
<th>di-E</th>
<th>mono-TAD</th>
<th>mono-E</th>
<th>Insoluble</th>
<th>Soluble</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.7</td>
<td>2.7</td>
<td></td>
<td></td>
<td>12</td>
<td>65</td>
<td>77</td>
</tr>
<tr>
<td>B</td>
<td>2.7</td>
<td>2.2</td>
<td></td>
<td></td>
<td>8</td>
<td>76</td>
<td>84</td>
</tr>
<tr>
<td>C</td>
<td>2.7</td>
<td>3.2</td>
<td></td>
<td></td>
<td>6</td>
<td>68</td>
<td>74</td>
</tr>
<tr>
<td>D</td>
<td>2.7</td>
<td>2.95</td>
<td>0.50</td>
<td></td>
<td>8</td>
<td>74</td>
<td>82</td>
</tr>
<tr>
<td>E</td>
<td>2.7</td>
<td>2.45</td>
<td>0.50</td>
<td></td>
<td>9</td>
<td>76</td>
<td>85</td>
</tr>
<tr>
<td>F</td>
<td>0.54</td>
<td>0.54</td>
<td></td>
<td></td>
<td>12</td>
<td>55</td>
<td>67</td>
</tr>
<tr>
<td>G*</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
<td></td>
<td>38**</td>
<td>49</td>
<td>87</td>
</tr>
</tbody>
</table>

Table IV: Concentration Effects on Yield of Soluble and Insoluble Polymer in Reaction of Bis-triazolinediones with Bis-enol Esters.

Temp. 0°, 15 hrs, 40°, 5 hrs.
*Temp 25°, 32 hrs, ethyl acetate,
**in CH₂Cl₂ only 10% of the total amount of polymer is insoluble.
concentration of the insoluble gel was found when an excess of diester was used. The highest yield of the soluble gel was in the experiment with an excess of triazolinodione. Probably the triazolinodione reacts in some kind of crosslinking reaction (second ene reaction, or decomposition). When an excess of the faster-consumed bis-triazolinodione is used, higher yields of polymer are formed.

The lower yield of soluble polymer at lower monomer concentration is probably due to the slower reaction rate. Different proportions between soluble and insoluble polymers in ethyl acetate solvent are the result of different solubilities of the polymer in both solvents (Eventually only 10% is insoluble in CH$_2$Cl$_2$). The insoluble polymer in CH$_2$Cl$_2$ solvent swelled in DMF but did not dissolve completely. The insoluble fraction in ethyl acetate was soluble in large amount of DMF.

The soluble polymers were analyzed by NMR and GPC. The molecular weights of the polymers were measured by VPO, and the intrinsic viscosities were also determined.

The NMR spectrum indicated the product to consist of more than 80% of the structure predictable for the 1,4-dipolar rearrangement product [43].

\[
\begin{align*}
\text{NMR spectrum indicated the product to consist of more than 80}\%\text{ of the structure predictable for the 1,4-dipolar rearrangement product [43].}
\end{align*}
\]

The GPC of all soluble polymers showed a strong signal at molecular weight $M \approx 1800$ indicating the presence of some species with strongly determined molecular weight - probably dimer ($M = 1268$) or trimer ($M = 1902$). Because the NMR did not show the end group in ratio 1:3 or 1:2 this oligomer can even be cyclic. In all samples, besides the oligomer, a broad signal for polymer is present at $M \approx 3000$. This broad peak moves to the lower molecular weight region when the concentration of comonomers is decreased and terminating agents are added. It moves to the higher molecular weight region ($M \approx 5000$) when an excess of bis-triazolinodione is used.

Viscosity measurements of these polymers were performed at 25° in DMF solvent and were similar: $[\eta] = 0.10 \pm 0.03$ dl/g. The inherent viscosity and ratio $\eta_{sp}/C$ were very close to each other ($k' - k'' = 0$) and almost independent of concentration. Such strange behavior suggests slightly polyelectrolyte (dissociation of $>\text{N-N-M bond}$) character.
Molecular weight measurements done in acetone by VPO were found to be 
$M = 1000$ for CH$_2$Cl$_2$ experiments and for polymer formed in ethyl acetate $M = 1260$.

The DSC analysis of all soluble polymers indicated decomposition to
begin at $190\pm5^\circ$ with the maximum rate of $237\pm5^\circ$C. The DSC analysis of the
ingurable polymers starts at $207\pm10^\circ$ with the maximum rate at $258\pm50^\circ$C.

| Table V: The Effect of Reaction Time and Dilution on the Reaction of
<p>| Bis-triazolinediones with Bis-enol Esters |</p>
<table>
<thead>
<tr>
<th>Exp</th>
<th>Conc $10^2$M</th>
<th>T, °C</th>
<th>t hrs</th>
<th>Insoluble</th>
<th>Soluble</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.56</td>
<td>2.56</td>
<td>20</td>
<td>74</td>
<td>56</td>
<td>36</td>
</tr>
<tr>
<td>B</td>
<td>0.60</td>
<td>0.60</td>
<td>20</td>
<td>700</td>
<td>32</td>
<td>55</td>
</tr>
<tr>
<td>C</td>
<td>2.50</td>
<td>2.75</td>
<td>20</td>
<td>72</td>
<td>54</td>
<td>39</td>
</tr>
<tr>
<td>D</td>
<td>2.56</td>
<td>2.56</td>
<td>0</td>
<td>700</td>
<td>54</td>
<td>34</td>
</tr>
<tr>
<td>E</td>
<td>2.56</td>
<td>2.56</td>
<td>20</td>
<td>700</td>
<td>61</td>
<td>28</td>
</tr>
<tr>
<td>F</td>
<td>2.56</td>
<td>2.56</td>
<td>70</td>
<td>22</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>G</td>
<td>2.56</td>
<td>2.56</td>
<td>20</td>
<td>23</td>
<td>43</td>
<td>46</td>
</tr>
</tbody>
</table>

1,5-Bis(1,2,4-triazoline-3,5-dionyl)naphthalene was reacted with
diisopropenyl adipate in ethyl acetate at 0°, 25°, 70°. The effect of
reaction time and dilution was also studied as shown in Table V.

The reaction was followed by UV and the rate constant of disappearance
of the triazolinedione signal and formation of polymer was found to be
equal. $K = 2.6\times10^{-3}$ mole$^{-1}$ l.s$^{-1}$ at 22° and the rate constant of the reaction
between isopropenyl acetate and phenyl-triazolinedione equals $K = 7.0\times10^{-3}$M$^{-1}$l.s$^{-1}$.

An increase of temperature increases the amount of insoluble polymer. 
Probably side reactions (second ene reaction and/or intermolecular dipole
coupling) have higher energy of activation than 1,4-dipolar rearrangement
and at higher temperature their contributions increase.

The yield of insoluble polymer also increases with the increase of reaction
time (at 25° after 23 hrs - 43%, 56% after 74 hrs, and 61% after 700 hrs).
indicating that some side reactions cannot be excluded.

A decrease of the concentration increases the yield of soluble polymers
by slowing down the second step which leads to insoluble products. An
excess of diester does not influence the yield of either product.

The ethyl acetate-insoluble part was almost completely soluble in DMF
making it possible to determine viscosity and make GPC analysis.

The ethyl acetate-insoluble polymers have intrinsic viscosities in
DMF at 25°, $[\eta] - 0.2-0.4$ dl/g, but the viscosity does not increase with
prolongation of the reaction time indicating that, the higher yields of
insoluble polymers at longer reaction times are not caused by the increase
of their molecular weights but rather by side reactions leading to insoluble
products (possibly highly polar urazole rings formed via the ene reaction). Molecular weights determined by GPC based on polystyrene calibration were in the range of $M \approx 5000$.

The ethyl acetate-soluble polymers had much lower viscosity ($[\eta] = 0.02-0.04 \text{ dL/g}$) and GPC analysis in $\text{CH}_2\text{Cl}_2$ solvent shows the pressure of a broad signal at approximately $M = 1000$. Number average molecular weights measured by VPO in acetone were in the range of $M = 700-1000$. The NMR of soluble fractions indicated that 1,4-dipolar rearrangement is the major reaction (80%).

The DSC measurements of insoluble polymers indicated slow decomposition at 195° with maximum rate at 253±2°C. For the soluble polymers decomposition starts at the same temperature with maximum rate at 251±5°C.

3. Bis(p,p'-1,2,4-triazoline-3,5-dimethylphenyl)methane was reacted with diisopropenyl adipate in nitromethane, ethyl acetate and methylene chloride at room temperature and concentration $[C]_0 = 9 \times 10^{-3} \text{ mole L}^{-1}$ for 48 hrs as shown in Table VI.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$C_1 = C_2 \times 10^2$</th>
<th>% Yield</th>
<th>Insoluble</th>
<th>Soluble</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{NO}_2$</td>
<td>0.9</td>
<td>16</td>
<td>78</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{OC(O)CH}_3$</td>
<td>0.9</td>
<td>15</td>
<td>78</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>0.3</td>
<td>0.5</td>
<td>94</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{OC(O)CH}_3$</td>
<td>3.3</td>
<td>48</td>
<td>48</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

The increase of concentration of both comonomers in ethyl acetate increases the yield of insoluble polymer from 15 - 48%. However half of it (24.4%) was found to be soluble in $\text{CH}_2\text{Cl}_2$ solvent as well as in $\text{CHCl}_3$. This gives possibility to fractionate the polymer. The methylene chloride-insoluble part was partially soluble and partially swelled in DMF indicating the presence of very polar groups (urazole) and some extent of crosslinking.

The polymers were analyzed by GPC and NMR. Viscosity and molecular weights by (VPO) were measured. The ethyl acetate-soluble part showed the presence of two peaks at $M = 2500$ and $M = 1260$. VPO (CHCl3) of the same sample gave $M = 1700$. Analysis of the NMR spectrum shows the presence of the following structure (H4):
and from the integration of the corresponding signals "\( \eta \)" could be calculated \((n - 3)\). Comparing this result with the GPC and VPO data we can conclude the presence of the tetramer and dimer – both terminated with unreacted ester groups \((M_{(n+2)} = 2578, M_{(2+2)} = 1402)\). The intrinsic viscosities measured in CHCl₃ and DMF at 25°, of the ethyl acetate-soluble sample were equal, \([\eta] = 0.065 \text{ dL/g}\). The ethyl acetate-insoluble CH₂Cl₂-soluble polymer had higher molecular weight: GPC \((M = 4000)\), VPO \((\text{CHCl}_3) (M = 4030)\). In the NMR spectrum the signals from the end group were not detected indicating higher molecular weights. The viscosity measured in DMF and CHCl₃ was also considerably higher, \([\eta] = 0.19 \text{ dL/g}\).

The polymers formed in nitromethane and methylene dichloride showed (GPC) lower molecular weights \((\text{CH}_2\text{Cl}_2: M = 2500 \text{ and } M = 750; \text{CH}_3\text{NO}_2: M = 1400)\). Also viscosities were much lower – polymer synthesized in CH₃NO₂ had \([\eta] = 0.037 \text{ dL/g} \text{ in DMF at 25°}\).

The IR of polymer insoluble in both CH₂Cl₂ and ethyl acetate showed strong absorption at 3500 cm⁻¹ in the range typical for >N–N–H band (Broad signal due to hydrogen bonds). This signal has much lower intensity in the sample soluble in CH₂Cl₂ and disappeared in the polymer soluble in ethyl acetate. These results indicate that the ene reaction and crosslinking process formed rather insoluble polymers and polymers with small contribution of the ene reaction are still soluble in CH₂Cl₂. The character of the viscosity-concentration dependences indicate the presence of some dissociation (>N–H⁺).

4. Another attempt to obtain polymers with good thermal properties was to use bis(triazolinediones) and styryl esters to form polymers by double Diels-Alder or Diels-Alder ene reactions. However, as one can expect from model studies the 1,4-dipolar rearrangement should lead in this case to termination and polymers with low molecular weights. The side reactions occurred in this case simultaneously leading to formation of crosslinked insoluble polymer in approximately 50% yield (depending on the structure of triazolinedione used). Another 50% consisted of soluble solid which had very low intrinsic viscosity \([\eta] = 0.015 \text{ dL/g}\) and molecular weight (GPC) to be less than \( M = 1000\).
5. Use of the "technical fraction" of distyryl terephthalate and isophthalate (70% pure) with \(4,4'\)-bis(1,2,4-triazoline-3,5-dionyl)-3,3'-dimethoxydiphenyl in CH\(_2\)Cl\(_2\) solvent lead to almost quantitative formation of an insoluble gel which was not further analyzed.

6. By changing the substituent of the \(\beta\) olefinic carbon atom we expected to slow down the Diels-Alder reaction and shift the course of the reaction towards rearrangement products. Bis(triphenylvinyl)terephthalate and \(4,4'\)-bis(1,2,4-triazoline-3,5-dionyl)-3,3'dimethoxydiphenyl were dissolved in CH\(_2\)Cl\(_2\) solvent at room temperature at \([C]_0 = 1.1 \times 10^{-2}\) mol l\(^{-1}\). Unfortunately steric hindrance introduced by the bulky phenyl groups decreased not only the Diels-Alder reaction but the rearrangement reaction as well. During 30 days, less than 5% of comonomers reacted. The rate constant is of the same magnitude as that for the decomposition of triazolinedione. Because of the poor solubility of the diester it cannot be performed at higher concentration and because of the instability of the triazolinedione at higher temperature it cannot be performed at higher temperature.

Structural Limitations and Tentative Conclusions

A 1,4-dipolar rearrangement reaction, which occurs between N-substituted-1,2,4-triazoline-3,5-diones and vinyl esters gives the possibility of formation of polymers with new and interesting structures when bis(triazolinediones) and enol esters of dibasic acids are used (45):

![Structural formula](image)

The \(R_4\) substituent connecting two triazolinedione molecules has only a small influence on the reaction pathway. When \(R_5 = (CH_2)_4\) (adipate esters) and \(R_2, R_3 = H, R_4 = CH_3\), the formula above describes the main structure of the polymer chain. When \(R_4 = phenyl\), instead of the rearrangement product, Diels-Alder and ene adducts dominate. When \(R_2, R_3, R_4 = phenyl\), reactivity of the ester due to large steric hindrances is negligible.

Polymers obtained from diisopropenyl adipate could be divided into two fractions. First fraction, insoluble in methylene dichloride and in most common organic solvents, is partially soluble in DMF and partially swollen in it. The IR of these polymers had strong broad absorption at 3500 cm\(^{-1}\) indicating the presence of >N-H bonds which are formed via the ene reaction. Crosslinking is an effect of secondary ene reaction, intermolecular dipole coupling and decomposition of triazolinedione ring. The viscosity of the samples partially soluble in DMF showed slight polyelectrolyte character (increase of \(\eta sp/C\) with decrease of \(C\), identical values of reduced and
inherent viscosities). The elemental analysis indicated higher content of triazolinedione than ester in the polymer. The yield of this fraction increases with an increase of triazolinedione: ester ratio and with temperature and reaction time. The molecular weight of that fraction soluble in DMF measured by GPC was \( M = 5000 \) (if calibration with polystyrene is valid for such highly polar polymers).

The second fraction of the polymers obtained is soluble in \( \text{CH}_2\text{Cl}_2 \) and consists of two kinds of polymers: oligomers which are in most cases terminated by unreacted ester groups and some higher polymer.

Oligomers are soluble in \( \text{CH}_2\text{Cl}_2, \text{CHCl}_3, \text{C}_2\text{H}_5\text{OC}(\text{O})\text{CH}_3, (\text{CH}_3)_2\text{CO} \) as they are mostly dimers, trimers, or tetramers. Their molecular weight varies from \( M = 2500 \) to \( M = 1000 \). VPO gives \( M = 1700 - 700 \). The viscosity of these polymers is less than \( [\eta] = 0.1 \text{ dL/g} \). The IR does not show the absorption at 3500 cm\(^{-1}\) indicating that 1,4-dipolar rearrangement products dominate. The elemental analysis shows much higher content of the ester units than triazolinedione units.

Higher polymers are insoluble in ethyl acetate and acetone but are soluble in dichloromethane. Molecular weight of this fraction is in the range \( M = 5000 - 3000 \). Some purer samples have the same molecular weights by VPO and GPC (\( M = 4000 \)). The nmr spectrum indicates that the end groups are not present. Viscosity is higher than for oligomers \( [\eta] = 0.2 \text{ dL/g} \) and show character typical for polyelectrolytes. The IR indicates the presence of \( >\text{N-H} \) bonds (peak at 3500 cm\(^{-1}\)) but the intensity of that peak is small in comparison with the insoluble fraction.

The yield of the soluble polymers decreases with a decrease of the TAD ester ratio and with decrease of temperature and decrease of the concentration of comonomers.

Differential scanning calorimetry (DSC) analysis of both samples (soluble and insoluble polymers) indicated the same behavior for all polymers. The decomposition starts at 200\( \pm 15^\circ \text{C} \) and the maximum rate is at 253\( \pm 5^\circ \text{C} \) (one at 237\( \pm 5^\circ \text{C} \)). These results indicate that the instability of the polymers is caused by the ester unit and by changing diisopropenyl adipate to some other ester more thermally stable polymers may be obtained.

The possibility of variation of the ester structure is not however too large. A phenyl substituent in the \( \alpha \)-position accelerates the reaction very much (more than 100 times) in comparison with methyl) but the reaction is not selective and Diels Alder products are mainly formed. Two phenyl substituents in the \( \beta \)-position eliminate the Diels Alder reaction but due to large steric hindrance also slow down the rearrangement process. The reaction occurs at the same rate as decomposition of the triazolinedione.

Other possibilities to improve the ester structure are to use substituted aromatic rings (elimination of Diels-Alder reaction) and halogenated vinyl esters. However the synthesis of such structures could be very difficult.

An increase in the stability of the products could conceivably be accomplished by changing the acid structure from adipate to oxalate, perhaloadipate or aromatic acids. However model studies indicate that
substitution of acetic acid by benzoic shifts the reaction from the direction of rearrangement to the intermolecular dipole coupling (crosslinking). The use of stronger acid (chloroacetate, trifluoroacetate) decreases the reaction rate and this has also to be remembered in the choice of the acid.

Conclusions:

Synthesis of a number of novel polymer structures via (1) the reaction of bis-triazolinediones with substituted styrenes, and (2) the reaction of bis-triazolinediones with bis-enol esters has been accomplished. However, because of the limited time available on the present phase of this investigation, the conclusions drawn must be considered to be tentative, and the investigation far from complete. Nevertheless, the results to date, while revealing and interesting from the standpoint of novel chemistry and chemical reactions, are not indicative that polymers having thermal stability in ranges beyond those presently available will be forthcoming from either of the approaches investigated. However, this does not necessarily imply that other uses for these novel systems could not be found. For example, the unusual reactivity of these polymers suggest that they may be useful for immobilizing chemically reactive species such as enzymes, insecticides, fungicides, etc., as well as for other uses dependent upon such reactive functional groups. Further consideration of any given structure, however, would require a specific effort directed toward attaining optimum properties such as molecular weight, molecular weight distribution, etc., for the required purpose.
### Personnel:

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<td>6/11/77 - 7/12/77</td>
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Bibliography


NOVEL POLYMER STRUCTURES VIA A 1,4-DIPOLAR REARRANGEMENT MECHANISM. I. Reaction of Bis-triazolinediones with Divinyl Esters.

Introduction

It has been shown by us (1,2) that vinyl esters (I) undergo an initial reaction with 4-substituted-1,2,4-triazoline-3,5-diones (II) to generate a 1,4-dipolar species. This reactive intermediate can produce stable, covalently-bonded products via three different pathways (Eq. 1):

\[ \text{Ia-d} + \text{IIa,b} \rightarrow \text{IIIa-d} \]

- **(a)** 1,4-Dipolar coupling
- **(b)** Diazetidine
- **(c)** 1,4-Dipolar rearrangement

\[ \text{a, } R = \text{CH}_3; \text{ b, } R = \text{CH(CH}_3)_2; \text{ c, } R = \text{C(CH}_3)_3; \text{ d, } R = \text{C}_6\text{H}_5; \text{ e, } R = \text{CH}_2\text{Cl.} \]
Vinyl ethers and 1,2,4-triazoline-3,5-diones (II) have been shown to copolymerize predominantly via route (a) (3). A kinetic study (2) of a variety of enol esters with IIb have shown that the distribution of products in Eq. 1 is strongly dependent upon electronic and steric factors in the ester (I). Energy of activation for dipole formation between IIb and Ia (vinyl acetate) is equal to 12 kcal/mole. In this case the distribution of products via routes (a), (b), and (c) is 7, 9, and 84%. When steric factors are introduced via R, as in vinyl isobutyrate (Ib) or vinyl pivalate (Ic), $E_a$ remains unchanged, but the product distribution via routes (a), (b), and (c), is now 15, 8, 77 and 16, 42, 42%, respectively. The $E_a$ for the reaction between IIb and vinyl benzoate (Id) is only slightly lower (11 kcal/mole), but again proportions between products are entirely different (87, 7, 6%, respectively). When strong electronic factors are introduced via R, e.g. chloroacetate (Ie), $E_a$ is increased to 14 Kcal/mole; however, the product of route (c) is then formed in 95% yield. Route (c) can be envisioned schematically as shown in Eq. 2:

\[
\begin{align*}
\text{Route (c)} & \\
\text{Eq. 2}
\end{align*}
\]
Thus it can readily be seen that when $R$ is an electron-withdrawing group (cation destabilizing) ($R = \text{CH}_2\text{Cl}$), $E_a$ for dipole formation is increased. However, when instead of H, $R''$ is introduced, which can be electron-releasing group (cation stabilizing) ($R'' = \text{CH}_3$, $\text{C}_6\text{H}_5$) $E_a$ for dipole formation should be reduced. 1,4-Dipolar rearrangement reaction for substituted vinyl esters and attempts to employ this reaction as polymer forming are described in our next papers. As can easily be seen from Eq. 2, where $R$ is very bulky, route (c) is hindered and routes (a) and (b) now become sterically favored routes for dipole disappearance.

As shown in Eq. 3, the dipolar rearrangement route (c) can become polymer forming when reaction occurs between a bis-vinyl ester of a dibasic acid (III) and a bis-triazolinedione (IV):

$$
\text{CH}_2=\text{C-OC}\{\text{CH}_2\}_4\text{C-OC}=\text{CH}_2 + \text{N}^\prime\text{Z-N=N-N} \to \\
\text{III} \quad \text{IV}_{a-b}
$$

$$a,Z=\{\text{O}\}-\text{CH}_2-\{\text{O}\}$$

$$b,Z=\{\text{CH}_2\}_6$$

Eq. 3

$$
\begin{bmatrix}
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O}
\end{bmatrix}
\to
\begin{bmatrix}
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O} \\
\text{CH}_2\text{N}^\prime\text{Z-N}^\prime\text{N}\text{O}
\end{bmatrix}
$$

$\text{V}_{a-b}$
Route (b) between III and IV is also polymer forming but it leads to polymer of different structure and stability. On the other hand, route (e) between III and IV is cross-linking. Therefore the proper polymerization conditions (solvent, temperature, concentrations, and ratios between comonomers) should be chosen so that route (c) is a favorable pathway for dipole disappearance. This letter describes our efforts to utilize Eq. 3 to yield novel linear polymer systems.

**Results and Discussion**

In attempts to employ the intramolecular rearrangement [Route (c), Eq. 1] as a mode of propagation for copolymerization, IVa and IVb were reacted with divinyl adipate [III], prepared by the reaction of vinyl acetate with adipic acid (4). Divinyl adipate was chosen as the diester because of its small steric hinderance and proper strength. Acids with shorter carbon backbones are stronger than adipic and should have higher energy of activation for the rearrangement process and should require much longer time to obtain polymers with high molecular weight. Because 4-substituted-1,2,3-triazolinediones are known to decompose slowly at room temperature (5), reaction should be completed fast enough to avoid decomposition of IV.

The copolymerization of IVa and III in tetrahydrofuran (THF) was studied both at room temperature and 60°, and in both cases the characteristic red color of the triazolinedione ring was discharged to light yellow while a light yellow opaque gel formed. The gel was filtered, and the filtrate was slowly added to a tenfold excess of hexane causing precipitation of an off-white solid. In both cases the yield of precipitated solid was less than 10% of the theoretical. The nuclear magnetic resonance (nmr) spectrum of the precipitate gave resonance signals at δ: 1.7 (multiplet, protons "a" in Va), 2.9 (multitplet, protons "b"), 4.1 (singlet, protons "c"), 4.7 (singlet, protons "d"), 7.4 (singlet, protons "e"), and 9.4 (singlet, protons "f").
Besides those signals, very broad ones were present at δ: about 6.0, 4.0, and 1.1 ppm δ indicating presence of units formed by routes (a) and (b) (Eq. 1) in less than 20% yield.

Comparison of this spectrum with the spectra of model compounds VI, prepared in 60% yield by reaction of IVa with two moles of vinyl acetate, and VII, synthesized in 80% yield by the reaction of III with two moles of IIb allowed the assignment of Va as the structural repeat unit for the copolymer.
Infrared (IR), NMR, and elemental analysis confirmed the assignment of the structure. Vapor pressure osmometry (VPO) in acetone gave a value of 1510 for the number average molecular weight (Mn) for the sample prepared at room temperature. In both the room temperature and the 60° copolymerization, the light yellow gel constituted greater than 80% of the theoretical yield and was insoluble in most organic solvents. Swelling was noted in dimethylformamide (DMF) and dimethylsulfoxide (DMSO), however. Although the IR spectrum was almost identical to the spectrum of the soluble copolymer, it was difficult to make a structural assignment based upon this evidence alone. A sample of the solid was heated to 60° for five hours in DMSO-d$_6$, dissolving 12% of the solid. NMR analysis was inconclusive, however, since it was possible that copolymer degradation could have occurred under these conditions.

The soluble, low molecular weight copolymer, Vb, resulting from the reaction of III with IVb in THF was also prepared at both room temperature and 60°. As before, no noticeable difference was detected by increasing the reaction temperature other than decreasing the time necessary for complete reaction. The major product of the copolymerization (>80%) was an insoluble gel. The soluble copolymer gave the following NMR spectrum, $\delta$: 1.5 (multiplet, "a"), 1.7 (multiplet, "b"), 2.9 (multiplet, "c"), 3.6 (multiplet, "d"), 4.7 (singlet, "e"), and 9.5 (singlet, "f" in Vb):
Some broad signals at 6.0, 3.9, and 1.1, corresponding to products formed by routes (a) and (b) (Eq. 1), were also present.

The model compound VIII and IX gave the following spectra:

Low molecular ($\overline{M_n} = 1830$ for sample prepared at room temperature) soluble polymer consisted of more than 80% of the structure shown in Vb. The structure was assigned by comparison of nmr spectra with model compounds VIII and IX.

THF was chosen as a solvent in the experiments described above because of higher solubility of bis-triazolinediones in this solvent than in others tried. On the other hand, the dipole formation, which was found to be the rate determining step in the dipolar rearrangement reaction, should occur faster in solvents of good solvating ability. The model studies performed in THF showed that reaction occurred in THF 10 times slower than in $\text{CH}_2\text{Cl}_2$. 
or $C_2H_2Cl_4$. The reason for such behavior is strong-solvation of the electron-deficient triazolinedione by THF molecules. This phenomenon can even be detected by a shift of the maximum of absorption of triazolinedione in THF in comparison with other "inert" solvents ($CH_2Cl_2$, $CHCl_3$, $C_6H_6$, $C_2H_4Cl_2$). This hypsochromic effect for the phenyl derivative (IIb) equals 13 nm ($543\rightarrow530$) and for the methyl derivative (IIa) it is 9 nm ($539\rightarrow529$ nm). More efficient solvation of the ground state prevents the dipole formation from increasing the free energy of activation in THF solvent. Moreover in THF there was much lower proportion of the main rearrangement product than in $CH_2Cl_2$ solvent, (50 and 84%, respectively). This can be explained by strong solvation of the intermediate acyloxy cation which increases steric hinderance, preventing rearrangement reaction and directing the dipole disappearance towards intermolecular dipolar coupling. The latter leads, in the case of bifunctional monomers, to insoluble, crosslinked polymer. By changing the solvent to methylene chloride or 1,2-dichloroethene, an increase of soluble polymer was obtained. When reaction between III and IVe was run in $CH_2Cl_2$ at $60^\circ$ or at room temperature the yield of insoluble polymer was in both experiments only 23% and soluble polymer was obtained in 68 and 69% yield, respectively. The nmr spectra were identical with those from THF solvent. When 1,2-dichloroethane was used as solvent at $60^\circ$, the yields of insoluble and soluble fractions were 30 and 62%, respectively. Slightly higher proportion of insoluble polymer in $C_2H_4Cl_2$ than in $CH_2Cl_2$ was caused by poorer solubility of the polymer in $C_2H_4Cl_2$. About 20% of insoluble polymer (in $C_2H_4Cl_2$) was soluble in $CH_2Cl_2$. Viscosity measurements performed in DMF at $25^\circ$ gave the values of intrinsic viscosities for polymers synthesized in $CH_2Cl_2$ at $25^\circ$, $60^\circ$, and $C_2H_4Cl_2$ at $60^\circ$: $[\eta] = 0.104, 0.109,$ and $0.078$ dl/g, respectively. The inherent and reduced viscosities were equal to each other and almost concentration independent.
The molecular weights were measured by GPC in C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} solvent using 10\textsuperscript{2} and 10\textsuperscript{3} Å columns. In CH\textsubscript{2}Cl\textsubscript{2} solvent there were two species present with molecular weights M = 2850 and M = 1700. The molecular weights correspond to pentamer and trimer. Polymer synthesized in C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} had two peaks at M = 2600 and M = 1500 based on polystyrene calibration. The nmr spectra showed that the polymers consisted of more than 80% of the structures described by Va. Less than 20% was formed probably by route (b). When the solution of polymer, after filtration from insoluble gel, was poured into hexane and the precipitated polymer dried at 60\textdegree/0.03 mm Hg, it was not completely soluble in CH\textsubscript{2}Cl\textsubscript{2} nor C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} nor even in DMF. Probably in the very non-polar medium the diazetidine ring can open and form some interchain bonds. This process could also occur during drying; however it was found that 1,2-diazetidine obtained in reaction between Ic and IIb did not decompose at 60\textdegree in CHCl\textsubscript{3} solvent during sixteen hours (5).

The differential scanning calorimetry (DSC) analysis showed the onset of decomposition of all polymers at 170±2\textdegree C with maximum for soluble polymers at 220±3\textdegree and for insoluble polymers over 250\textdegree C.

The reaction between III and IVb in CH\textsubscript{2}Cl\textsubscript{2} at room temperature yielded 57% of insoluble and 34% of soluble polymers. The higher yield of insoluble fraction, when an aliphatic substituent was chosen in IV instead of aromatic one, was established by model studies. The product distribution by routes (a), (b), and (c) was 7, 9, 84%, and 10.5, 5.5, 84%, respectively when phenyl (IIb) and methyl (IIa) triazolinediones reacted with vinyl acetate in C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} solvent at 60\textdegree. The proportion of product by route (e) increases from 7 to 10.5% when the aromatic substituent is replaced by an alkyl group. The yield of insoluble fraction when bifunctional monomers were used increased from 23 to 57%. The insoluble gel can be formed by intramolecular dipolar coupling as a result of the attack on the negatively charged nitrogen or oxygen atom.
(see Eq. 1). In the second case C=N bond should be formed. The ir spectra of insoluble polymers showed the presence of absorption at 1610 cm\(^{-1}\) typical of the C=N bond. Nevertheless, the intensity of this peak was rather small in comparison with polymers formed by reaction of vinyl ethers with triazolinediones where C=N bonds were present to a much larger extent (3).

The copolymerization conditions, polymer properties, and analyses of the soluble polymers obtained from bis-triazolinediones and divinyl adipate are shown in Table 1.

**Conclusions**

The yield of soluble, linear polymer of novel structure described by formula V varies from 5 to 70% depending on the connecting unit in IV, solvent and monomer concentrations; influence of temperature is of minor effect. When aromatic substituents are used in IV and solvents non-interacting with II the yield of soluble polymer of M = 2000 and \([\eta]_{\text{DMF}}^{25^\circ} = 0.10\ \text{d}l/g\) is about 70%. The polymer still contains a small amount of the intramolecular dipolar coupling products [routes (b) and (c) in Eq. 1)] which can decompose and form insoluble polymer in very low yield. DSC analysis indicates the onset of decomposition at 170±2°C for both soluble and insoluble fractions.

**Experimental**

**Synthesis of Intermediates**

Divinyl adipate (III) was synthesized according to a previously described procedure (4). The triazolinediones (IIa, b, and IV a, b) were synthesized according to previously published procedures (1-3).

**Synthesis of Model Compounds**

Model Compound VI: To a solution of IVa (0.112 g, 3.1\times10^{-4}\ \text{mole}) in 40 ml of \(\text{CH}_2\text{Cl}_2\), solution of Ia (0.106 g, 1.24\times10^{-3}\ \text{mole}) in 10 ml of \(\text{CH}_2\text{Cl}_2\) was slowly added. The red solution was stirred at room temperature overnight. The following morning the solution was yellow indicating that the reaction was complete. The solution was slowly added to 250 ml of petroleum ether precipitating 0.148 g of white solid. The nmr spectrum (\(\text{DMSO-d}_6\)) showed
### Table 1

**Copolymerization Conditions, Polymer Properties, and Analyses of Soluble Polymers from Bis-triazolinediones and Vinyl Adipate**

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<th>Polymer Number</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Concentration x10² M</th>
<th>Total %</th>
<th>Insoluble %</th>
<th>Soluble %</th>
<th>M GPC</th>
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<td>Vb</td>
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*Measured by VPO (acetone)
this solid to be 80% pure VI. The other 20% consisted of products formed by
routes (a) and (b) (Eq. 1). The solid was partially soluble in CHCl₃. The
CHCl₃ solution was added to 200 ml of petroleum ether precipitating 0.101 g
(61% yield) of white solid melting at Mp = 135°, which was found by nmr to be
more than 95% pure VI.

Model Compound VII: III (0.113 g, 5.7x10⁻⁴ mole) was dissolved in 10 ml of
C₂H₄Cl₂ and was slowly added to 40 ml solution of IIb (0.200 g, 1.14x10⁻³
mole). The red solution was stirred at 60°C during 15 hours. The yellow
solution was slowly added to 250 ml of petroleum ether precipitating 0.289 g
(92%) of white solid, Mp = 105°, which was found by nmr to be 90% pure VII.
Attempts to purify the sample by column chromatography were unsuccessful.

Model Compound VIII: To a solution of IVb 10.098 g, 3.5x10⁻⁴ mole in 40 ml
of C₂H₄Cl₂ solution of Ia (0.120 g, 1.4x10⁻³ mole) in 10 ml of C₂H₄Cl₂ was slowly added. After stirring for 14 hours at 60° the solution turned
from red to yellow color. The solution was added slowly to 250 ml of
petroleum ether precipitating 0.143 g (90% yield) slightly yellow solid.
The solid was dissolved in CHCl₃ and reprecipitated from petroleum ether.
The yield was 0.113 (71%) of white solid which was found by nmr (CDCl₃)
to be more than 95% pure VIII.

Model Compound IX: Solution of III (0.103 g, 5.2x10⁻⁴ mole) in 10 ml of
C₂H₄Cl₂ was slowly added to 40 ml solution of IIa (0.118 g, 1.04x10⁻³ mole). The solution after stirring for 24 hrs. at 60° turned yellow. Precipitation
in 250 ml of petroleum ether yielded 0.194 (87%) of slightly yellow solid
which was found by nmr to be more than 90% pure.

Typical Copolymerization Procedures

Divinyl adipate, III (0.000829 mole, 0.164 g) was dissolved in 15 ml
of THF and slowly added to a 20 ml solution of IVa (0.000829 mole, 0.330 g).
The solution was placed in a thick-walled glass tube, degassed by two liquid
nitrogen freeze-thaw cycles and sealed under vacuum. The red solution was
allowed to stand at room temperature until the characteristic red color
of IVa had changed to light yellow, a period of two days. During that time
a light yellow gel formed. The gel was filtered and washed with THF, followed
by drying overnight at 58°/0.03 mm, to give a light yellow solid weighing
0.380 g (32%). The solid was found to be insoluble in chloroform, acetone,
benzene, methylene chloride, nitromethane, water, 1,4-dioxane, ethyl acetate,
carbon disulfide, acetonitrile, and hexamethylphosphorotriamide. The solid
was observed to swell considerably in DMSO and DMF, but did not melt or
soften at temperatures up to 250°; instead, it slowly darkened if left at
temperatures greater than 200° for more than 15 minutes. Ir (KBr): 3450 (m, b),
3300 (m, b), 2950 (m, b), 2950 (w, b), 1800 (m), 1720 (s, b), 1610 (w),
1600 (w), 1510 (m), 1420 (m, b), 1350 (w), 1220 (w), 1130 (w), 1020 (w), and
750 (w) cm\(^{-1}\). A 0.200 g sample was heated at 60° for 5 hours in DMSO-\(d_6\) dis-
solving 12% of the solid. Very broad nmr signals were located at \(\delta 1.7, 3.2,
4.2, 4.7,\) and 7.4. This sample was slowly added to 10 ml of water precipi-
tating a light yellow solid. Ir gave a spectrum almost identical to the origi-
nal insoluble solid.

Anal. Calcd. for a 1:1 copolymer, \(C_{27}H_{24}N_6O_8\): C, 57.86; H, 4.32; N, 19.99.
Found: C, 55.81, H, 4.43; N, 16.08.

The light yellow liquid, separated from the gel by filtration, was slowly
added to 200 ml of hexane precipitating 0.041 g (9%) of a light yellow solid,
which softened around 120°. The solid was soluble in CH\(_2\)Cl\(_2\), CHCl\(_3\), acetone,
DMSO, and DMF. Vapor pressure osmometry (VPO) in acetone gave a number average
molecular weight of 1510. Infrared absorbances were found at (KBr): 3500 (m, b),
3300 (m, b), 2980 (w), 1800 (m), 1730 (s, b), 1610 (w), 1600 (w), 1540 (w),
1500 (m), 1420 (m), 1350 (m), 1210 (w), 1130 (m), 1010 (w), and 750 (w) cm\(^{-1}\).
Nmr (DMSO-\(d_6\)) \(\delta\): 1.7 (m), 2.9 (m), 4.1 (s, broad), 4.7 (s, broad), 7.4 (s,
broad), and 9.4 (s, broad). Anal. Calcd for a 1:1 copolymer, \(C_{27}H_{24}N_6O_8\):
C, 57.86; H, 4.32; N, 14.33. Found: C, 57.00; H, 4.92; N, 14.39.

The other experiments were performed by the same procedure. In chlorinated solvents, concentrations of comonomers were equal and kept in the range of $(1.0 \pm 0.11 \times 10^{-2}$ mole $1^{-1}$.

References


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Vinyl esters (I) react with 4-substituted-1,2,4-triazoline-3,5-diones (II) generating 1,4-dipolar species (III). This intermediate decomposes by intra or intermolecular coupling (a) or can rearrange (b) forming 1-formyl methyl-2-acyl-1,2,4-triazolidine-3,5-diene (IV) (1, 2):

\[
R^1\text{-C-O-C=CH}_2 + \text{II} \rightarrow \text{III} \rightarrow \text{IV}
\]

\[\text{II} \rightarrow \text{III}\]

\[\alpha, R=\text{CH}_3\]
\[\beta, R=\text{C}_6\text{H}_5\]

An \(\alpha\)-alkyl substituent in the vinyl ester should stabilize the dipolar species and lower the energy of activation of its formation (rate determining step). The presence of an \(\alpha\)-substituent should also shift the dipole decomposition towards rearrangement (route (b)). Indeed, when H was substituted by \(\text{CH}_3\) group in acetate ester the energy of activation
was reduced from 12 to 7.5 kcal/mole$^{-1}$ and the reaction rate increased at room temperature about 50 times (1). The contribution of route (a)(Dipole coupling) decreased from 16 to less than 2%.

Triazolinediones are among the most powerful dienophilic (3) and enophilic (4) reagents known. In reaction products between isopropenyl acetate (Ia) and triazolinediones (II), in addition to the expected rearrangement product (V), the ene product (VI) was also found:

\[
\begin{align*}
\text{II}_a,b & \quad + \quad \text{Ia} \\
& \quad \xrightarrow{K_R} \quad \text{V} \\
& \quad \xrightarrow{K_E} \quad \text{VI}
\end{align*}
\]

Both products were simultaneously and directly observed during their formation by nmr technique. Eventually they were separated and characterized (see Experimental).

Rate constants and proportions of ene product are shown in Table 1. 4-Phenyl substituted triazolinedione (IV) is about 50% more reactive than the methyl derivative (IIa) and for IIb the reaction is shifted more in the direction of the rearrangement product. Lower values of rate constants in more polar and better solvating solvents are rather surprising for the proposed highly polar intermediate. THF or acetonitrile
should solvate the dipole, lowering $E_a$. Analysis of the UV spectra has shown that THF, ethyl acetate, and acetonitrile interact strongly with triazolinedione and that the energy level of the ground state is in that case decreased more than the energy level of the transition state. Such a phenomenon leads to an increase in the energy of activation and slows down the reaction rate. The shift of the absorption maximum for IIA equals to 9 nm for THF, CH$_3$CN, and C$_2$H$_5$OC(0)CH$_3$ ($\lambda_{max} = 529$ nm) in comparison with CH$_2$Cl$_2$, CHCl$_3$, or C$_6$H$_6$ ($\lambda_{max} = 538$). The blue shift for IIB equals to 13 nm ($\lambda_{max} = 530$ and 543 nm respectively). This shift was even greater for the more polar DMSO (for IIA $\lambda_{max} = 521$) and the reaction was still slower in that solvent (Table 1).

The values of the rate constants of ene reaction when compared with the ene reaction for simple olefin [e.g. for IIB and 1-hexene $k_E = 2.9 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ in benzene at 22°C (5)] indicates that ene reaction and the rearrangement reaction proceed by different mechanisms. If both of them proceeded via the dipolar intermediate the ester group (dipole stabilizing) should lower the energy of activation for the ene reaction between II and the enol ester. Thus the rate constants for the reaction between II and olefin should be much smaller but they are not. This observation also indicates that the ene reaction goes through a converted or biradical mechanism (4).

The ene product VI is not thermodynamically stable and can slowly rearrange to V:
The reverse reaction is rather unlikely because the 1-acetyl-methyl-2-acetyl-4-substituted-1,1,4-triazolidine-3,5-dione (V) is much more stable, while VI contains the easily hydrolyzable enol ester bond.

The reaction described in Eq. 3 occurs relatively fast in highly polar solvents as DMSO ($k = 2 \times 10^{-5} \text{s}^{-1}$ at $22^\circ$) and much slower in less polar CHCl$_3$ ($k < 10^{-6} \text{s}^{-1}$ at $22^\circ$). Addition of silica gel increases the rate of the reaction. When the reaction was run with non-dried solvents also 1-acetyl methyl-2yl-4-substituted-1,2,4-triazolidine-3,5-dione (VII) was formed:
Because the conversion of the ene product to the rearranged product was much slower than the reactions between II and Ie (Eq. 2), the ratio between V and VI was almost constant during reaction. The rate constants $k_R$ and $k_E$ were calculated by extrapolation of the V, VI ratio to the initial reaction state.

The ene product (V) still has double bonds and allylic hydrogen atoms and has potential ability to participate in the next ene reaction with one more triazolinedione molecule. Model studies (5) however, have shown that the second ene reaction for linear olefin is several times slower than the first addition.

Rearrangement and ene reactions can become polymer forming when diisopropenyl esters (VIII) and bis-triazolinediones (IX) are used:

\[
\text{CH}_2=\text{C}-\text{O}-\text{C}-(\text{CH}_2)_4-\text{O}-\text{C}=\text{CH}_2 \quad \text{VIII}
\]

\[
\text{N} \quad \text{Z} \quad \text{N} \quad \text{O}-\text{C}=\text{CH}_2 \quad \text{IX a-d}
\]

\[
an, \text{Z} = (\text{CH}_2)_6 \\
b, \text{Z} = (\text{O})\text{CH}_2(\text{O}) \\
c, \text{Z} = (\text{O})\text{CH}_3 \\
d, \text{Z} = (\text{O})\text{CH}_3
\]

\[
\begin{bmatrix}
\text{CH}_3 \\
\text{C} = \text{O} \\
\text{CH}_2 \\
\text{C}=\text{O} \\
\end{bmatrix}
\]

\[
\begin{bmatrix}
\text{N} \quad \text{Z} \quad \text{N} \\
\text{O} \quad \text{C}=\text{CH}_2 \\
\text{V} \quad \text{a-d} \\
\text{n}
\end{bmatrix}
\]

Eq. 4
The proper choice of the bifunctional connector units (Z in IX), solvent and temperature can direct the reaction towards the rearrangement route and formation of the polymer with structure described by formula X in Eq. 4. The second ene reaction or the intermolecular dipolar coupling [route (a) in Eq. 1] should lead to the formation of insoluble, cross-linked polymer. Compensation for the extent to which crosslinking proceeds can be accomplished by employing an appropriate ratio of the comonomers or additions of monofunctional monomers (Ia) and (II). Properly chosen temperature, solvent, structure of IX, and stoichiometric balance between comonomers and Ia and II, would lead to linear polymers of potential usefulness. This paper describes our efforts to obtain novel polymer systems (X) from these sources.

**Results and Discussion**

In attempts to employ the intramolecular rearrangement [route (b), Eq. 1] as a mode of propagation for copolymerization, different bis (triazolinonediones) (IX) were reacted with diisopropenyl adipate (VIII). The copolymerizations were studied in different solvents, at different temperatures and with different comonomer ratios. In all cases the characteristic red color of the triazolinonedione was discharged to light yellow while a light opaque gel formed. The precipitate was filtered, and the filtrate was slowly added to a tenfold excess of hexane causing precipitation of an off-white solid. When IXa and VIII were reacted in THF the yield of precipitated solid was less than 10% of the theoretical. The nmr
spectrum of the precipitate gave resonance signals at δ: 1.5 (m, 8, protons "a"), 1.7 (m, 4, "b"), 2.1 (s, 6, "c"), 3.0 (m, 4, "d"), 3.6 (m, 4, "e"), and 7.8 ppm (s, 4, "f").

Comparison of this spectrum with the spectra of model compounds XI prepared in 65% yield by reaction of IXe with two moles of isopropenyl acetate, and XII, synthesized in 68% yield by the reaction of VIII with two moles of Ixe allow the assignment of Xa as the structural repeat unit for the copolymer. Ir, nmr, and elemental analysis confirmed the assignment of the structure. VPO measurement in acetone gave a value of 1780 for the number average molecular weight (Mn).
The light yellow gel constituted greater than 80% of the theoretical yield and was insoluble in most organic solvents. Swelling was noted in dimethylformamide (DMF) and dimethylsulfoxide (DMSO), however. A sample of the solid was heated to 60° in DMSO-\textsubscript{d}\textsubscript{6} for five hours, and about 10% of the solid was solubilized. NMR analysis was inconclusive, however, since it was possible that copolymer degradation could have occurred under these conditions. Because 4-allyl substituted triazolinediones are less selective in rearrangement reactions (see Table I and Ref. 2) the aromatic connecting units (2 in IX) were used in all following experiments.

The results of the copolymerization of VIII and IX\textsubscript{b} are presented in Table II. The proportion of soluble polymer increases rapidly when solvent is changed from THF to ethyl acetate, nitromethane, or \textsubscript{CH}_{2}\textsubscript{Cl}. Model studies for isopropenyl acetate (Ia) indicate absence of intermolecular dipole coupling [route (a) Eq. 1]. Adipic esters can participate in cross-linking to a larger extent than acetates because the proportion of intermolecular dipole coupling (cross-linking) increases with the size of the RCOO group (I). THF, which is known from its high solvating abilities can solvate the intermediate dipole (III) increasing steric hinderence, thus preventing rearrangement and directing the reaction towards route (a). Even a small ratio of intermolecular dipolar coupling in a polymerization reaction would chemically bond the copolymer chains forming the crosslinked, insoluble gel. The increase of concentration of comonomers increases the amount of insoluble polymer because the proportion of intermolecular to intramolecular coupling depends on concentration.
The soluble polymers were analyzed by nmr and ir. Molecular weights were estimated by gpc, vpo and viscosity measurements.

The gpc of the polymer soluble in ethyl acetate indicated presence of two peaks at $M = 2500$ and $M = 1300$. Number average molecular weight ($\bar{M}_n$) measured in CHCl$_3$ (VPO) of the same sample was equal to $M = 1700$. The nmr spectrum of that polymer, besides the main peaks also showed that signals from the unreacted ester groups were present:

![NMR spectrum diagram](image)

The chemical shifts were as follows (ppm $\delta$): $a$ (1.70, m); $b$ (1.75, m), $c$ (1.90, s), $d$ (2.15, s), $e$ (2.40, m), $f$ (2.95, m), $g$ (4.05, s), $h$ (4.65, m), $i$ (4.85, s), $j$ (7.35, m). Integration of the corresponding signals gave the value for "n" ($n = 3$). Comparison of this result with gpc and vpo data enabled us to conclude the presence of tetramer and dimer, both ended with unreacted ester groups ($M_{TE} = 2578$, $M_{DE} = 1402$).

The intrinsic viscosities measured in CHCl$_3$ and DMF at 25$^\circ$ were equal, $[\eta] = 0.065$ dl/g. The polymer (insoluble in ethyl acetate, but soluble in CH$_2$Cl$_2$) had higher molecular weight:
gpc_{CH_2Cl_2} (M = 4000), vpo_{CHCl_3} (M = 4000). The signals from the end groups were not detected in the nmr spectrum indicating higher molecular weights. The viscosities measured in DMF and CHCl_3 were also considerably higher ([\eta] = 0.19 d1/g).

The polymers formed in nitromethane, methylene chloride, or THF had lower molecular weights. Gpc of polymer formed in CH_2Cl_2 had two peaks at M = 2500 and M = 750, while polymer formed in CH_3NO_2 indicated one peak at M = 1400. Mn of the polymer formed in THF was 1400. Also viscosities were much lower - polymer formed in CH_3NO_2 had [\eta] = 0.037 c1/g in DMF at 25°.

The ir of the polymer insoluble in both CH_2Cl_2 and ethyl acetate showed strong broad absorption at 3500 cm^-1 in the range typical for >N-N-H band (hydrogen bonding). This signal had much lower intensity for the sample which was soluble in CH_2Cl_2 and almost disappeared in the polymer which was soluble in ethyl acetate.

These results indicate that the ene reaction and cross-linking formed rather insoluble polymers while polymers with only a small amount of the ene product are still soluble in CH_2Cl_2. The character of the viscosity-concentration dependences indicate the presence of some dissociation (>N-H^-)

The influence of the comonomer ratio and addition of some terminating compounds (monofunctional comonomers) and the reaction products were studied in copolymerization of diisopropenyl adipate (VIII) and 4,4'-bis(1,2,4-triazoline-3,5-dione)-3,3'-dimethoxy diphenyl (IXc). The reaction was followed until the typical red color of triazolinodione disappeared. The results of these experiments are summarized in Table III.
In \( \text{CH}_2\text{Cl}_2 \) solution the lowest amount of the insoluble gel was formed when an excess of the diester was used. The highest yield of the soluble gel was in the experiment with an excess of bis(triazolinedione). Triazolinedione reacts in some kind of crosslinking reaction (secondary ene reaction, intermolecular dipolar coupling, condensation). When an excess of the faster consumed bis(triazolinedione) was used higher yields of polymer were observed. The lower yield of soluble polymer at lower concentration was probably due to incomplete reaction. Different proportions between soluble and insoluble polymers in ethyl acetate and in \( \text{CH}_2\text{Cl}_2 \) resulted by different solubilities of the polymer in the solvents (eventually only 10% is insoluble in \( \text{CH}_2\text{Cl}_2 \)). The insoluble polymer formed in \( \text{CH}_2\text{Cl}_2 \) swelled in DMF but did not dissolve completely indicating presence of a small amount of crosslinking. The fraction insoluble in ethyl acetate was soluble in a large amount of DMF. Thus, the proportion of the intermolecular dipolar coupling in that solvent was the lowest, similar to the copolymerization of VIII and IXb.

The soluble polymers were analyzed by nmr. The spectrum indicated that polymer is formed via the 1,4-dipolar rearrangement reaction to an extent greater than 80%.
The following chemical shifts were observed (ppm \( \delta \)):
a \((1.75, \text{m})\), b \((2.15, \text{s})\), c \((2.95, \text{m})\), d \((3.9, \text{s})\), e \((4.85, \text{s})\),
f \((7.2, \text{m})\). The gpc of all soluble polymers showed a sharp
signal at molecular weight \( M = 1800 \) indicating the presence
of some species with strongly determined molecular weight -
probably dimer \((M = 1268)\) or trimer \((M = 1902)\). Because in
nmr there were no signals from the end group in the ratio 1:2 or
1:3, this oligomer could even by cyclic. In all samples,
besides the oligomer, a broad signal for polymer was present
\((M = 3000)\), which moved to the lower molecular weight region
when the concentration of comonomers was decreased and also
when terminating agents were added. It moved to the higher
molecular weight region \((M = 5000)\) when an excess of bis(tri-
azolinedione) was used. Viscosities of all polymers measured
in DMF at 25\(^{\circ}\) were within a narrow range, \([\eta] \pm 0.10 \pm 0.03 \text{ dl/g} \). 
Both inherent and reduced viscosities were similar and almost
independent of concentration. Such strange behavior suggests
a low degree of polyelectrolyte (dissociation at \(>\text{N-H}\) bond of the
ene product) character.

Molecular weights measured by Vpo in acetone for the poly-
mers formed in all experiments were in the range from \( M = 1000 \)
to \( M = 1300 \).

The dsc analysis of all soluble polymers indicated decom-
position to begin at \(190 \pm 50\) with the maximum rate at \(237 \pm 5^{\circ}\)C.
The decomposition of insoluble polymers starts at \(207^{\circ} \pm 10^{\circ}\)
with the maximum rate at \(258 \pm 5^{\circ}\)C.

1-5-Bis(1,2,4-triazoline-3,5-dionyl)naphthalene (IXd) was
reacted with VIII in ethyl acetate at 0\(^{\circ}\), 25\(^{\circ}\), and 70\(^{\circ}\). The
effect of reaction time and dilution was also studied. The
results are presented in Table IV. The reaction was followed by ultraviolet (UV) spectrometry. The rate constant for disappearance of the triazolinedione signal at \( \lambda = 535 \text{ nm} \) (polymer formation) was found to be equal to \( k = 2.6 \times 10^{-3} \text{M}^{-1} \text{s}^{-1} \) at 22°C. The rate constant of the reaction between Ia and IIb is almost exactly of the same magnitude: \( k = 2.0 \times 10^{-3} \text{M}^{-1} \text{s}^{-1} \) (see Table 1).

The increase of temperature enhanced the amount of insoluble polymer. The crosslinking reactions (secondary ene reaction, intermolecular dipolar coupling, condensation of the triazolinedione ring) have higher activation energy than 1,4-dipolar rearrangement and their contributions at higher temperature increase. The yield of insoluble polymer also increased with reaction time (at 20°, 43% after 23 hrs, 56% after 74 hours and 61% after 700 hrs.), indicating the presence of some slow secondary crosslinking reaction. The decrease of the comonomer concentrations increased the yield of soluble polymers apparently by slowing down the secondary crosslinking step. An excess of diester did not influence the yield of either product.

The ethyl acetate-insoluble polymer was soluble in DMF making it possible to determine viscosity and conduct GPC analysis. The ethyl acetate-insoluble polymers had intrinsic viscosity equal to \( \left[ n \right] = 0.3 \pm 0.1 \text{ d}l/g \) in DMF at 25°. The viscosity did not increase with prolongation of the reaction time. This result indicates that not an increase of the molecular weight but rather, side reaction (perhaps formation of highly polar urazole rings via the ene reaction) is responsible for the insolubility of the polymers. Molecular weights determined
by GPC (DMF) based on polystyrene calibration were in the range $M = 5000$.

The soluble polymers had much lower viscosity ($[\eta] = 0.03 \pm 0.01 \text{ d}l/\text{g}$) and the GPC analysis in CH$_2$Cl$_2$ showed the presence of a broad signal at approximately $M = 1000$. $\bar{M}_n$ measured by VPO in acetone were in the range $M = 700 - 1000$. The nmr spectra of soluble fractions showed that 1,4-dipolar rearrangement is the major propagation reaction (>80%).

The following chemical shifts were observed: 1.75 (a, m), 2.20 (b, s), 2.90 (c, m), 4.90 (d, s), 7.70 (e, m), 8.30 (f, m).

The dsc analysis of both insoluble and soluble polymers indicated slow decomposition to begin at $195^\circ$ with maximum rate at $251^\circ \pm 5^\circ C$. 
Conclusions

Polymers obtained in the copolymerization of diisopropenyl adipate (VIII) and different bis(triazolinediones) can be divided into two fractions. The first fraction is insoluble in CH₂Cl₂ and partially swollen and partially soluble in DMF. A strong signal at 3500 cm⁻¹ is present in the ir of these polymers indicating presence of >N-H bonds resulting from an ene reaction. Also very weak absorption at 1610 cm⁻¹ was observed due to C=N bond. The C=N bond can be formed in an intermolecular dipolar coupling reaction as a result of attack of positively charged carbon atom on carbonyl from triazolinedione molecule. Similar products were also found where II reacted with vinyl ethers.⁶ The intensity of the 1610 cm⁻¹ absorbance was very low. Thus, the extent to which intermolecular coupling proceeded is believed to be small. Elemental analysis of these polymers showed higher proportions of IX than for 1:1 copolymer. Triazolinediones cannot homopolymerize⁷ at room temperature but probably two consecutive additions are still possible. Such a reaction should also increase the proportion of crosslinking. Yield of the insoluble fraction increased with temperature, reaction time and concentration. Slow solubilization of the polymer in DMF can be due to the conversion of ene structures to rearrangement (Eq. 3) or hydrolysis of ene products and formation of linear copolymers. The viscosity of these polymers were comparatively high ([n] = >0.2 d1/g DMF, 25°) and molecular weights were in the range of M = 5000.

The second part was a linear polymer soluble in CH₂Cl₂. It still could be separated into oligomers soluble in ethyl acetate and acetone and somewhat higher polymer insoluble in
these solvents. The oligomeric fraction consisted mostly of dimers, trimers, and tetramers often with unreacted ester groups at both ends. Viscosity was less than \([\eta] = 0.1\) dL/g in CHCl₃ at 25°C. Gpc gave values of molecular weights from \(M = 1000\) to \(M = 2500\). Vpo showed a lower range of molecular weights \(M = 700 - 1700\). No 3500 cm\(^{-1}\) ir absorbtion was present. Also the 1610 cm\(^{-1}\) absorbance was absent.

The polymer which was insoluble in ethyl acetate but soluble in CH₂Cl₂ had a weak ir peak at 3500 cm\(^{-1}\) indicating a small proportion of ene structure. Nmr showed no signals from end groups indicating the polymer was of higher degree of polymerization. These polymers had molecular weights from \(M = 3000\) to \(M = 5000\) (gpc). \(M_n\) (VPO) (\(M = 4000\)) were also considerably higher than those of oligomers. Viscosities were in the range of \([\eta] = 0.2\) dL/g in DMF or CHCl₃ at 25°C. The yield of this fraction increased with decrease of temperature, reaction time, concentration, and IX:VIII ratio; a larger portion of soluble fraction was formed when aromatic instead of aliphatic connector units (Z) were used in the bis(triazolinediones) (IX).

**Experimental**

Diisopropenyl adipate (VIII) was synthesized according to a previously described procedure. The triazolinediones, II and IX, were synthesized according to previously published procedures.

**Synthesis of Model Compounds**

1-Acetyl)1-methyl-2-acetyl-4-phenyl-1,2,4-triazoline-3,5-dione (Vb) and 1-(2-acetoxy-1-propene-3-yl)-2-yl-4-phenyl-1,2,4-triazoline-3,5-dione VIb) were obtained in the reaction
of equimolar amounts of Ia and IIb in CH$_2$Cl$_2$ solvent at room temperature ([Ia]$_0$ - 0.1 mole x l$^{-1}$). The ratio of Vb to VIb in the oil after evaporation of solvent was 89 to 11. Both products were separated by column chromatography on silica gel using CHCl$_3$ as a solvent. Vb was recrystallized from benzene-petroleum ether solvent pair in 75% yield as white crystals, mp = 130-131°. Nmr (CDCl$_3$) $\delta$: 2.16 (s, 3), 2.58 (s, 3), 4.82 (s, 2), 7.48 (s, 5).

Anal. Calcd for C$_{13}$H$_{13}$N$_3$O$_4$: C, 56.73; H, 4.73; N, 15.27. Found: C, 56.83; H, 4.80; N, 15.33.

VIb was crystallized from benzene-petroleum ether solvent pair in 7% yield as white crystals, mp = 123°. NMR (CDCl$_3$) $\delta$: 2.18 (s, 3), 4.25 (s, 2), 5.12 (m, 2), 7.45 (s, 5), 7.8 (broad, 1). Mass spectrum gave a parent peak at m/e 275.

Anal. Calcd. for C$_{13}$H$_{13}$N$_3$O$_4$: C, 56.73; H, 4.73; N, 15.27. Found: C, 56.70; H, 4.89; N, 15.32.

When VIb was stirred in methanol-chloroform solvent pair in presence of silica gel in an open flask overnight, 1-acetyl-methyl-2-yl-4-phenyl-1,2,4-triazoline-3,5-dione (VIIb) was formed in 35% yield. Vb was formed in 55% yield. VIIb was separated on a silica gel column using CHCl$_3$:CH$_3$OH (20:1) solvent pair and recrystallized from CH$_2$Cl$_2$-hexane mixture as white crystals, mp = 127°C (yield 10%). NMR (CDCl$_3$) $\delta$: 2.21 (3, s), 4.45 (s, 2), 6.0 (broad, 1), 7.45 (s, 5). Mass spectral analysis gave a parent peak at m/e 233 and an intense peak at 190 (loss of CH$_3$CO). Anal. Calcd. for C$_{11}$H$_{11}$N$_3$O$_3$: C, 56.65; H, 4.72; N, 18.03. Found: C, 56.42; H, 4.79; N, 18.12.
1-Acetyl methyl-2-acetyl-4-methyl-1,2,4-triazolidine-3,5-dione (Va) and 1-(2-acetoxy-1-propene-3-yl)-2-yl-4-methyl-1,2,4-triazolidine-3,5-dione (Vie) were formed in CH₂Cl₂ at room temperature ([Ie]₀ = 0.1 mole l⁻¹) in 85:15 ratio. Va was crystallized from benzene-petroleum ether mixture in 76% yield as white crystals. Nmr (CDCl₃) δ: 2.16 (s, 3), 2.58 (s, 3), 3.17 (s, 3), 4.84 (s, 2). Mass spectrum gave a parent peak at m/e 213. Anal. Calcd. for C₅H₁₁N₃O₄: C, 45.07; H, 5.16; N, 19.72. Found: C, 45.62; H, 5.19; N, 19.58.

Vie was very poorly soluble in benzene and was recrystallized from CH₂Cl₂-hexane in 10% yield as white crystals, mp = 115°C. Nmr (CDCl₃) δ: 2.16 (s, 3), 3.08 (s, 3), 4.16 (s, 2), 5.10 (m, 2), 7.75 (broad, 1). Mass spectrum gave a parent peak at m/e 213. Anal. Calcd. for C₈H₁₁N₃O₄: C, 45.07; H, 5.16; N, 19.72. Found: C, 45.53; H, 5.01; N, 19.75.

Model Compound XI: IXa (0.00125 mole) was dissolved in 50 ml CH₂Cl₂ and was slowly added to a 20 ml solution of Ia (0.00251 mole). The red solution was stirred overnight at room temperature. The slightly yellow solution was precipitated in hexane. The precipitate was extracted with benzene reprecipitated in petroleum ether, and dried at 60°C/0.03 mm overnight. The yield was 65%. Nmr (DMSO-d₆) δ: 1.43 (m, 4), 2.13 (s, 3), 2.53 (s, 3), 3.62 (m, 2), 4.82 (s, 2) which was consistent with the assigned structure XI.

Model Compound XII: IIa (0.00254 mole) was dissolved in 50 ml of CH₂Cl₂ and was slowly added to a 20 ml solution of VIII (0.00127 mole). The red solution was stirred overnight. The slightly yellow solution was precipitated in petroleum ether. The solid was extracted with benzene,
reprecipitated in petroleum ether, and dried overnight at 60°/0.03 mm. The yield was 68%. Nmr (DMSO-d$_6$) δ:

1.60 (m, 2), 2.12 (s, 2), 2.90 (m, 2), 3.16 (s, 3), and 4.78 (s, 2), which was consistent with the assigned structure XII.

The copolymerization procedure was the same as published before. Molecular weights were measured at 37° on 302 Mechrolab Vpo. Gpc measurements were performed on "Waters" instrument using 10$^2$, 10$^3$, 10$^4$ Å μ-Styrogel column with CH$_2$Cl$_2$ solvent and 10$^3$, 10$^4$ Å with DMF solvent.
### Table 1

Rate Constants of Rearrangement and ene Reaction between Isopropenyl Acetate (IIe) and Triazolinediones (II)

<table>
<thead>
<tr>
<th>R</th>
<th>t °C</th>
<th>Solvent</th>
<th>$k_r \text{ M}^{-1}\text{s}^{-1} \cdot 10^2$</th>
<th>$k_e \text{ M}^{-1}\text{s}^{-1} \cdot 10^3$</th>
<th>$\Sigma_S \text{ M}^{-1}\text{s}^{-1} \cdot 10^2$</th>
<th>% E</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>35</td>
<td>CDCl$_3$</td>
<td>3.2</td>
<td>5.3</td>
<td>3.7</td>
<td>15</td>
<td>nmr</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>35</td>
<td>C$_6$D$_6$</td>
<td>1.2</td>
<td>1.7</td>
<td>1.4</td>
<td>12</td>
<td>nmr</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>35</td>
<td>CH$_3$NO$_2$</td>
<td>0.6</td>
<td>1.8</td>
<td>0.8</td>
<td>23</td>
<td>nmr</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>22</td>
<td>DMSO</td>
<td>---</td>
<td>---</td>
<td>0.06</td>
<td>---</td>
<td>UV</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>22</td>
<td>THF</td>
<td>0.2</td>
<td>0.17</td>
<td>0.21</td>
<td>8</td>
<td>UV*</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>35</td>
<td>CDCl$_3$</td>
<td>4.5</td>
<td>5.6</td>
<td>5.1</td>
<td>11</td>
<td>nmr</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>35</td>
<td>C$_6$D$_6$</td>
<td>1.8</td>
<td>1.8</td>
<td>2.0</td>
<td>9</td>
<td>nmr</td>
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<tr>
<td>C$_6$H$_5$</td>
<td>22</td>
<td>C$_6$H$_6$</td>
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<td>1.4</td>
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<tr>
<td>C$_6$H$_5$</td>
<td>22</td>
<td>CH$_3$C≡N</td>
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<td></td>
<td>UV</td>
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<tr>
<td>C$_6$H$_5$</td>
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<td>EtOAc</td>
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<td>UV</td>
</tr>
</tbody>
</table>

*Proportion of both products were determined after completion of the reaction and the rate constants calculated on that basis.
Table II

Yields of polymers in copolymerization of VIII and IXb

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$[\text{IXb}]_0 = [\text{VIII}]_0 \times 10^2 \text{M}$</th>
<th>Yield of Polymer %</th>
<th>[IXb]/[VIII] Ratio in Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>Soluble</td>
</tr>
<tr>
<td>THF</td>
<td>5.1</td>
<td>89</td>
<td>8</td>
</tr>
<tr>
<td>THF*</td>
<td>5.7</td>
<td>88</td>
<td>6</td>
</tr>
<tr>
<td>CH$_3$NO$_2$</td>
<td>0.9</td>
<td>94</td>
<td>78</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0.9</td>
<td>95</td>
<td>94</td>
</tr>
<tr>
<td>CH$_3$CO$_2$C$_2$H$_5$</td>
<td>0.9</td>
<td>93</td>
<td>78</td>
</tr>
<tr>
<td>CH$_3$CO$_2$C$_2$H$_5$</td>
<td>3.3</td>
<td>96</td>
<td>48</td>
</tr>
</tbody>
</table>

All polymerization were carried out at room temperature except

*(60°)*

**Half of this amount (24.4%) of the total is soluble in CH$_2$Cl$_2$ and the rest is partially swollen and partially soluble in DMF solvent.

§Calculated from elemental analysis
Table III
Yields of Polymers in Copolymerization of VIII and IXc

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp, °C</th>
<th>[IXc] $10^2$M</th>
<th>[VIII] $10^2$M</th>
<th>[IIb] $10^2$M</th>
<th>[Ia] $10^2$M</th>
<th>Total</th>
<th>Soluble</th>
<th>Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
<td>2.7</td>
<td>2.7</td>
<td></td>
<td></td>
<td>77</td>
<td>65</td>
<td>12</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
<td>2.7</td>
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<td></td>
<td></td>
<td>84</td>
<td>76</td>
<td>8</td>
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<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
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<td>3.2</td>
<td></td>
<td></td>
<td>74</td>
<td>68</td>
<td>6</td>
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<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
<td>2.7</td>
<td>2.95</td>
<td>0.50</td>
<td></td>
<td>82</td>
<td>74</td>
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</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
<td>2.7</td>
<td>2.45</td>
<td>0.50</td>
<td></td>
<td>85</td>
<td>76</td>
<td>9</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0*</td>
<td>0.54</td>
<td>0.54</td>
<td></td>
<td></td>
<td>67</td>
<td>55</td>
<td>12</td>
</tr>
<tr>
<td>CH$_3$COOC$_2$H$_5$</td>
<td>RT</td>
<td>2.4</td>
<td>2.4</td>
<td></td>
<td></td>
<td>87</td>
<td>49</td>
<td>38**</td>
</tr>
</tbody>
</table>

*15 hrs at 0°, then 5 hrs at 40°.

**38% is the amount of polymer insoluble in CH$_3$COOC$_2$H$_5$. Only 10% of polymer is insoluble in CH$_2$Cl$_2$ which is, on the other hand, completely soluble in DMF.
Table IV

Yields of Polymers in Copolymerization of VIII and IXd in Ethyl Acetate

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Time, n</th>
<th>[IXd]₀ Mx10^2</th>
<th>[VIII]₀ Mx10^2</th>
<th>Total</th>
<th>Soluble</th>
<th>Insoluble</th>
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<tr>
<td>20</td>
<td>74</td>
<td>2.56</td>
<td>2.56</td>
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<td>36</td>
<td>56</td>
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<tr>
<td>20</td>
<td>700</td>
<td>0.60</td>
<td>0.60</td>
<td>87</td>
<td>55</td>
<td>32</td>
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<td>20</td>
<td>72</td>
<td>2.50</td>
<td>2.75</td>
<td>93</td>
<td>39</td>
<td>54</td>
</tr>
<tr>
<td>0</td>
<td>700</td>
<td>2.56</td>
<td>2.56</td>
<td>88</td>
<td>34</td>
<td>54</td>
</tr>
<tr>
<td>20</td>
<td>700</td>
<td>2.56</td>
<td>2.56</td>
<td>89</td>
<td>28</td>
<td>61</td>
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<td>70</td>
<td>22</td>
<td>2.56</td>
<td>2.56</td>
<td>95</td>
<td>30</td>
<td>65</td>
</tr>
<tr>
<td>20</td>
<td>23</td>
<td>2.56</td>
<td>2.56</td>
<td>89</td>
<td>46</td>
<td>43</td>
</tr>
</tbody>
</table>
References


5. S. Ohashi and G.B. Butler, in preparation


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Kenneth B. Wagener
George B. Butler
Linear polymers of potentially good thermal stability could be formed via a 1,4-dipolar rearrangement process from bis-enol esters of dibasic acids and bis-(triazolinediones). Unsubstituted vinyl esters participate in intramolecular or intermolecular dipole coupling in addition to the rearrangement process (1, 2). The latter reaction for diesters and bis-(triazolinediones) lead to formation of insoluble crosslinked polymer. An α-methyl substituent in the ester stabilizes the intermediate dipole and decreases the energy of activation of the rearrangement reaction (1, 3). The enophilic character of triazolinediones is responsible for, parallel to rearrangement, the ene reaction. A phenyl substituent instead of methyl should also stabilize the dipole but should exclude the ene reaction (absence of allyl protons). When α-acetoxy styrene was used as the enol ester [1] in reaction with 4-methyl and 4-phenyl 1,2,4-triazoline-3,5-diones (IIa and IIb) besides the 1,4-dipolar rearrangement route the Diels Alder reaction occurs simultaneously:

\[ \text{Eq. 1} \]

![Chemical structure diagram](image)
The first Diels Alder adduct (IV) is very reactive and reacts immediately with another molecule of II in two parallel reactions: the ene reaction or a second Diels-Alder addition:

\[ IV + II \rightarrow V \]

The ene product (V) is not stable and it loses a molecule of HOC(O)CH₃ to form stable product VII. The reaction occurs through the carbocation which can be detected by conductivity to the appearance of its UV absorption (460 nm).
When different bis(triazolinediones) were reacted with I in molar ratio 1:1 two products were formed. Soluble oligomeric ($\bar{M}_n<1000$; $[\eta]<0.02$ d1/g) products as a result of terminating rearrangement reaction and insoluble polymer due to some decomposition reaction (2, 3) (condensation of triazolinedione rings, intermolecular dipole coupling).

Another attempt in the way of synthesis of linear polymers was to introduce into vinyl group three phenyl groups making Diels Alder reaction less probable. When bis(triphenyl vinyl)terephthalate was used as diester in reaction with VIIIa the rate of the disappearance of the VIIIa (measured by UV; $\lambda=530$ nm) was equal to the rate of decomposition of triazolinedione (4). Apparently three bulky phenyl groups prevent not only Diels-Alder but the rearrangement reaction.

Triazolinediones had too high dienophilic character (5, 6) to be successfully used in synthesis of linear polymers via intramolecular rearrangement with aryl substituted divinyl esters.
Experimental

Materials: Triazolinediones (II, VIII) were synthesized according to earlier published procedures (1, 2). α-Acetoxystyrene was formed in a transesterification reaction between acetophenone and isopropenyl acetate (7). α-Benzoxystyrene was synthesized from 0.15 mole of benzoyl dichloride and 0.30 mole acetophenone in 1 mole of triethylamine. The reaction mixture, after reflux for 24 hours, was dissolved in diethyl ether. Ammonium chloride was extracted with water and the organic layer was dried over Na₂SO₄. After distilling the unreacted acetophenone and benzoyl chloride, the residue was purified by chromatography on an alumina column using benzene as a solvent. The first fraction was distilled after removal of benzene and a fraction boiling at 130°/0.3 mm was collected. The oily distillate which solidified on standing was recrystallized from petroleum ether as colorless crystals, mp = 39°C.

Found: C, 80.58; H, 5.42.

Distyryl terephthalate was synthesized in a similar manner replacing 0.15 mole of benzoyl chloride by 0.07 mole of terephthaloyl chloride. The first treatment on alumina column with benzene gave 70% pure distyryl terephthalate. Attempts to crystalize the diester were unsuccessful. After two more purifications on alumina column the distyrl terephthalate was obtained as a brown oil which solidified. The purity as checked by nmr was more than 80%. In copolymerization studies with VIIIa 80% pure distyryl terephthalate was used. In CH₂Cl₂ solvent at concentration 10x10⁻² mole/l, the red color of triazolinedione disappeared after one hour. Insoluble gel was formed in 98% yield.

Bis(triphenylvinyl)terephthalate was formed from the corresponding potassium enolate and terephthaloyl chloride in diglyme dried over Na/K alloy. The enolate was formed in diglyme from potassium amide and triphenylethanol (8).
Before addition of the enolate solution to the aryl chloride solution very careful removal of ammonia was necessary \((10^{-2} \text{ mm Hg})\). After dropwise addition of the enolate solution under argon atmosphere, the mixture was stripped for 3 hrs until a white precipitate was formed. The solid was insoluble in water but soluble in a large amount of \(\text{CHCl}_3\). After drying the \(\text{CHCl}_3\) solution over \(\text{MgSO}_4\) and evaporation, the solid was recrystallized from \(\text{CH}_2\text{Cl}_2\) giving white crystals in 30% yield, melting at 258°C, being pure \(\alpha\)-acylated product. Present in solution was the \(\gamma\)-acylated product and a mixed ene. The mass spectrum of bis(methylvinyl)terephthalate gave a parent peak at \(m/e\) 674, which was 18% as intense as the base peak \((m/e\ 403)\). Other fragments were observed at \(m/e\) 271 (74%), 243 (38%), 165 (48%), 132 (29%), 105 (40%), 104 (52%), 77 (15%).

\text{Anal Calcd for C}_{48}\text{H}_{34}\text{O}_4: C, 85.46; H, 5.04.}

\text{Found: C, 85.35; H, 4.97.}

Attempts to copolymerize bis(triphenylvinyl)terephthalate with VIIIa at concentration \(1 \times 10^{-2} M\) in \(\text{CH}_2\text{Cl}_2\) at room temperature were unsuccessful. The rate of disappearance of triazolinedione absorption was equal to the rate of thermal decomposition of triazolinediones and no diester reacted.

\text{Reaction between I and IIa in benzene at room temperature: The solution of 0.70 g (43 mmole) of I in 5 ml of benzene was added to a solution of 0.48 g (43 mmole) of IIa in 45 ml of benzene. After 2 minutes, the red color changed to orange and an orange precipitate was formed. The filtrate was condensed on a rotary evaporator and the oily residue was twice recrystallized from a petroleum ether-\(\text{CH}_2\text{Cl}_2\) mixture to give white crystals, \(M_p = 121^\circ\text{C}\) in 22% yield. The mass spectrum gave a parent peak at \(m/e\) 275. The following peaks were also observed of intensity greater than 10% of the base peak at \(m/e\) 105: 233 (53%), 128 (81%), 77 (42%), 71 (17%), 43 (5%). The \text{nmr} spectrum confirmed the structure of the rearrangement product (IIla), 1-benzoylmethyl-2-acetyl-4-methyl-1,2,4-triazolidine-3,5-dione as shown in}
When the precipitate was left in open air the orange color rapidly disappeared. The same was observed upon dissolving in CH$_2$Cl$_2$ or DMSO. Eventually the precipitate was crystallized from DMSO giving white crystals in 10% yield. The crystals decompose upon melting above 250°C. The mass spectrum showed the parent peak at m/e 328 (0.6%) and a base peak at m/e 115. The nmr confirmed the structure of the Diels-Alder ene adduct VIIa (R = CH$_3$).

The NMR data are presented in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{13}$H$</em>{13}$N$_3$O$_4$</td>
<td>C, 56.73; H, 4.73; N, 15.27.</td>
<td>C, 56.19; N, 4.73; N, 15.38.</td>
</tr>
<tr>
<td>C$<em>{14}$H$</em>{12}$N$_4$O$_4$</td>
<td>C, 51.22; H, 3.66; N, 25.61.</td>
<td>C, 50.87; H, 3.59; N, 26.02.</td>
</tr>
</tbody>
</table>

Yield of the double diels-Alder adduct (VI) in benzene was negligible (Table 1).

Reaction between I and IIb in benzene at room temperature was performed according to the above procedure. 1-Benzoylmethyl-2-acetyl-4-phenyl-1,2,4-triazolidine-3,5-dione (IIIb) was crystallized in 19% yield (Mp - 139°C). The mass spectrum gave a parent peak at m/e 337. The following peaks are also present: m/e - 295 (62%), 190 (89%), 120 (51%), 119 (42%), 105 (100%), 77 (52%), 43 (60%). The nmr data are shown in Table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{18}$H$</em>{15}$N$_3$O$_4$</td>
<td>C, 64.09; H, 4.45; N, 12.46.</td>
<td>C, 64.18; H, 4.69; N, 12.53.</td>
</tr>
</tbody>
</table>

The Diels-Alder-ene product (VIIb) was recrystallized in 7% yield from DMSO. The crystals decomposed upon melting above 250°C. The mass spectrum gave a very weak parent peak at m/e 452. The base peak was observed at m/e 175.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{24}$H$</em>{16}$N$_6$O$_4$</td>
<td>C, 63.72; H, 3.54; N, 18.58.</td>
<td>C, 63.21; H, 3.41; N, 18.93.</td>
</tr>
</tbody>
</table>
Reaction between I and IIa in CH$_2$Cl$_2$ solvent at -78°C: To a stirred solution of 1.12 g (64 mmole) of IIa in 90 ml of CH$_2$Cl$_2$ at -78°C a solution of 1.04 g (64 mmole) of I in 10 ml of CH$_2$Cl$_2$ was slowly added. The red color disappeared after 3 days leaving a colorless solution which contained some insoluble white crystals. Upon warming to room temperature, the solution turned orange. A precipitate which formed upon pouring the filtrate into petroleum ether was recrystallized three times from a CCl$_4$-CH$_2$Cl$_2$ mixture giving pure double Diels-Alder adduct VIA in 7% yield. The white crystals decompose upon melting above 250°C. The mass spectrum gave a weak parent peak at m/e 388. The following major peaks were also observed at m/e: 346 (10%), 231 (14%), 146 (13%), 115 (87%), 105 (13%), 58 (100%), 43 (75%). NMR data are shown in Table 2.

Anal Calcd. for C$_{(16+16)}$H$_{16}$N$_6$O$_6$: C, 49.48; H, 4.12; N, 21.65.

Found: C, 49.48; H, 4.31; N, 21.66.

The first precipitate consisted of a mixture of VIA, VIIa and some condensation products of IIa. The filtrate was composed of unreacted I and rearrangement product IIIa.

Reaction between I and IIb in CH$_2$Cl$_2$ solvent at -78°C: The reaction was carried out according to the procedure described above. The red color disappeared after 1 day at -78°C. The double Diels-Alder adduct VIIb was obtained in 9% yield after two recrystallizations from CCl$_4$-CH$_2$Cl$_2$ mixture. Decomposition was observed upon melting above 250°C. The mass spectrum gave a very weak parent peak at m/e 512. The following major peaks were also observed at m/e: 470 (30%), 293 (19%), 119 (100%), 146 (23%), 177 (30%), 105 (25%), 91 (30%), 77 (25%). NMR data are shown in Table 2.

Anal. Calcd. for C$_{(26+20)}$H$_{20}$N$_6$O$_6$: C, 60.94, H, 3.91; N, 16.41.

Found: C, 60.17; H, 3.94; N, 16.67.
### Table 1

**Yields of Products of Reaction between α-Acetoxystyrene (I) and Triazolinediones (II) at 1:1 ratio**

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Solvent</th>
<th>T, °C</th>
<th>Ce10^2 M</th>
<th>Unreacted</th>
<th>Yields^a, %</th>
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<td></td>
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<td></td>
<td>I</td>
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</tr>
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<td>CH₂Cl₂</td>
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<td>0.7</td>
<td>39</td>
<td>22</td>
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<tr>
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<tr>
<td>7</td>
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<td>C₆H₆</td>
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<td>11.3</td>
<td>36</td>
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<td>CH₂Cl₂</td>
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<td>26.0</td>
<td>47</td>
<td>7</td>
</tr>
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</table>

^a Found by nmr analysis of crude mixtures; Calculated relative to starting ester.

^b α-Benzoxystyrene was used instead of I.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR Data for Compounds: III, VI, and VII</th>
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<td>$^1$H Chemical Shifts (ppm)</td>
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<tr>
<td></td>
<td>$^1$H NMR Data for Compounds: III, VI, and VII</td>
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</tbody>
</table>

Table 2
The first precipitate was composed of condensation products of IIb and a mixture of VIb and VIIb. Unreacted I and IIIb were present in the filtrate.

References


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Synthesis of Bis-(Triazolinediones)

The following bis-(triazolinediones) have been synthesized as indicated in the general synthesis scheme shown:

General Synthesis Scheme:

\[
\begin{align*}
\text{O=C=N-R-N=C=O} & \quad + \quad 2 \text{H}_2\text{NHC} & \quad \rightarrow \\
\text{CH}_3 & \quad \text{or} & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
0 &= \text{R} = \\
\text{or} & \\
\text{or}
\end{align*}
\]
Synthesis of Polymers

![Chemical Structure]

Although the polymers have not been completely characterized, previous evidence permits us to postulate that the styrene polymer contains both the repeating units resulting from (1) the double Diels-Alder reaction sequence and (2) the alternating Diels-Alder-ene reaction sequence in an approximate ratio of 1:2, while the p-chlorostyrene polymer probably possesses only repeating units derived from the alternating Diels-Alder-ene reaction sequence.

Synthesis of Divinyl Esters

A literature survey covering the available methods for synthesis of enol esters has been completed and methods are now being investigated in the laboratory for synthesis of the following ester:

![Chemical Structure]

In the meantime, divinyl succinate and divinyl adipate are being studied in their polymerization reactions with bis-(triazolinediones) in order to establish the relative importance of the side-reactions: (1) 2 + 2 cycloaddition of the intermediate dipolar species, a terminating reaction, and (2) the dipolar coupling reaction between the intermediate dipolar species, a cross-linking reaction. Proper balance between these two
competitive processes and the major dipolar rearrangement reaction must be attained in order to obtain useful polymers.

Acquisition of Chemical Intermediates

A variety of aromatic diamines and dicarboxylic acids have been acquired as chemical intermediates to be utilized as follows in synthesis of important reactants for the polymers:

1. \( H_2N-Ar-NH_2 + 2 \text{COCl}_2 \rightarrow O=C-N-Ar-N=C=0 \)

2. \( \text{HO-C-Ar-C-OH} \rightarrow \text{ClC-Ar-C-Cl} \rightarrow 2 \text{N}_3^\text{-} \)

3. \( \text{HOArCOH} \rightarrow \text{Several steps} \rightarrow \text{CH}_2=C-O-C-Ar-C-O-C=CH_2 \)

R = H, Alkyl or Aryl