

# POLYCYCLOTIMERIZATION AS A GENERAL ROUTE TO POLYMERS WITH RINGS IN THE CHAIN

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## ABSTRACT

Polycyclotrimerization is put forward as a new route to the synthesis of polymers of various structures containing carbo- or hetero-cyclic rings in the chain. Examples are described to indicate typical results. The wide possibilities in terms of selecting initial monomers thus provide a means of preparing a variety of polymeric structures. Since investigations in this field have barely begun, the potential of the method is yet to be determined. Nevertheless, we can expect that further studies will reveal considerable new synthetic possibilities for polycyclotrimerization which will contribute further to the chemistry of synthetic polymers.

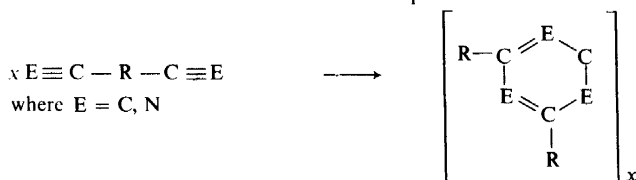
Until recently polymerization reactions were largely accomplished by the breaking of double or triple bonds, such as double and triple carbon-carbon bonds and carbonyl groups, or by cleavage of heterocyclic rings, *e.g.* epoxides or lactams.

Thus, in order to prepare polymers containing various rings in the chain, it was necessary to use monomers containing such rings.

However, in the last few years a number of articles have been published concerning polymerization reactions based on carbo- or hetero-cycle formation, *e.g.* Diels-Alder<sup>1</sup> polymerization and 1,3-dipolar polyaddition<sup>2</sup>. Some papers have described trimerization reactions of compounds containing acetylenic triple bonds<sup>3</sup>, nitrile groups<sup>4</sup>, cyanate<sup>5</sup>, and isocyanate groups<sup>6</sup>.

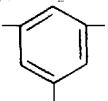
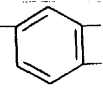
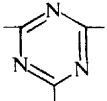
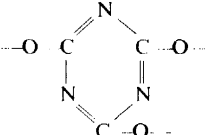
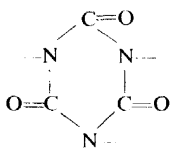
This paper deals with polycyclotrimerization reactions principally based upon the formation of aromatic carbo- and hetero-cycles by linking together three multiple bonds with subsequent ring-closure to a six-membered ring. These reactions may give rise to polymers which contain in the polymeric chain rings that are not present in the monomer. This obviously extends the synthetic possibilities of polymer chemistry.

Polycyclotrimerization reactions can be represented as follows:



Here, the monomer residues incorporated in the resulting macromolecule are linked together in six-membered carbo- and hetero-cyclic rings formed during the polycyclotrimerization. *Table 1* shows the groups which can be used in polycyclotrimerization.

*Table 1.* Groups participating in polycyclotrimerization

Group	Starting compounds containing this group	Type of polymer formed	Rings formed
$\text{--C}\equiv\text{C--}$	Diacetylenes	Polyphenylenes	 and 
$\text{--C}\equiv\text{N}$	Dinitriles	Poly-s-triazines	
$\text{--O--C}\equiv\text{N}$	Dicyanates	Polycyanurates	
$\text{--N=C=O}$	Di-isocyanates	Polyisocyanurates	

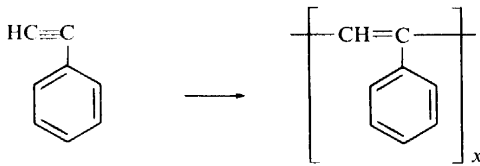
There have as yet been no systematic studies aimed at using such reactions in polymer synthesis, but there are now sufficient data to characterize various polycyclotrimerization reactions and to permit us to generalize them and consider this new branch of synthetic polymer chemistry as a whole.

### CHARACTERISTICS OF POLYCYCLOTRIMERIZATION REACTIONS

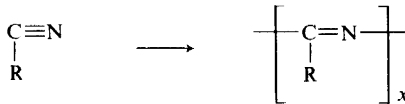
The great interest in linear polymerization is one of the reasons for the fact that polycyclotrimerization reactions have been disregarded by investigators for so long. Indeed, all the monomers used in polycyclotrimerization can be polymerized to give linear polymers, and it is precisely this feature which has been the principal subject of investigation.

Thus, the polymerization of monoacetylenes yields polyvinylenes<sup>7</sup>:

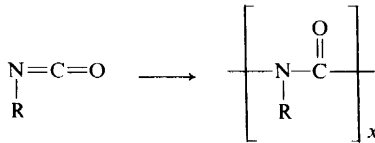
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Polymers with conjugated double bonds are also formed from nitriles<sup>8</sup>:

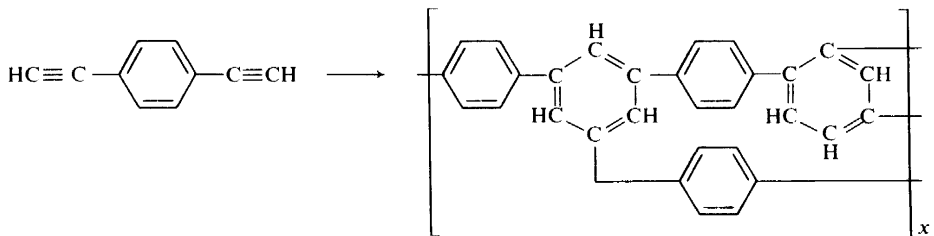


The polymerization of isocyanates leads to the formation of polyamides of the Nylon 1 type<sup>9</sup>:



This property of the types of monomers mentioned above has been investigated, and should be borne in mind when one is studying polycyclotrimerization reactions and the resulting compounds, since in this case the formation of linear structures is an undesired side-reaction. An important feature of polycyclotrimerization is the fact that in the preparation of polymers from monomers containing two or more multiple bonds, three-dimensional structures arise, which are often infusible and insoluble structures, and this presents certain difficulties in their examination and application.

In the case of polycyclotrimerization of di-acetylenes, for example *p*-diethynylbenzene, the reaction can be illustrated as follows<sup>10</sup>:

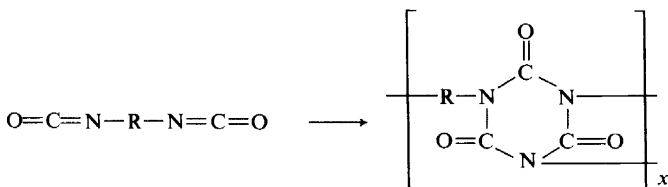


The rings formed in this reaction are a mixture of 1,2,4- and 1,3,4-substituted benzenes<sup>10,11</sup>, the ratio of these isomeric forms depending upon the catalyst and reaction conditions. In most cases the 1,2,4-substituted rings predominate<sup>11</sup>. Complex compounds of cobalt, nickel, titanium, and other metals, for example  $[(\text{C}_2\text{H}_5\text{O})_3\text{P}]_4\text{CoBr}$ ,  $(i\text{-C}_4\text{H}_9)_3\text{Al}$ ,  $\text{TiCl}_4$  and others, are used as catalysts<sup>10, 12-16</sup>.



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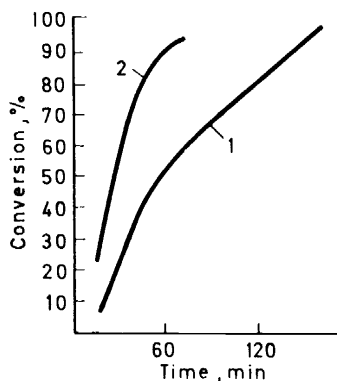
giving a three-dimensional polycyanurate<sup>19, 24</sup>. The polycyclotrimerization of di-isocyanates leads to three-dimensional polyisocyanurates<sup>6, 25</sup>:



Amines,  $\text{ZnCl}_2$ , and other salts, as well as various complex compounds (ferrocene, iron pentacarbonyl, and others) have been used as catalysts<sup>18, 25</sup>.

### KINETICS OF THE REACTION

Polycyclotrimerization of diethynylbenzene is a rather rapid first-order reaction. *Figure 1* illustrates the rate of diethynylbenzene conversion<sup>17, 19</sup>.



*Figure 1.* Rate of polycyclotrimerization of *p*-diethynylbenzene (catalyst concentration: 1— $2.0 \times 10^{-2}$ ; 2— $4.0 \times 10^{-2}$  mole/l).

As seen from this figure, in the presence of a catalytic system  $[(\text{C}_2\text{H}_5\text{O})_3\text{P}]_4\text{-CoBr}_2$  the reaction proceeds for 1–2 h, with total consumption of the monomer.

Polycyclotrimerization of 2,2-di-(4-cyanatophenyl)propane proceeds readily in the presence of tertiary amines, as shown in *Figure 2*.

As seen from this figure, the more basic tertiary amines are more active<sup>19</sup>.

The influence of temperature on polycyclotrimerization of 2,2-di-(4-cyanatophenyl)propane is clearly seen from *Figure 3*. The conversion increases with temperature, and at 250–300°C the monomer is almost fully converted into polymer<sup>19</sup>.

### REACTION MECHANISM

Polycyclotrimerization proceeds as a bimolecular process, in which a

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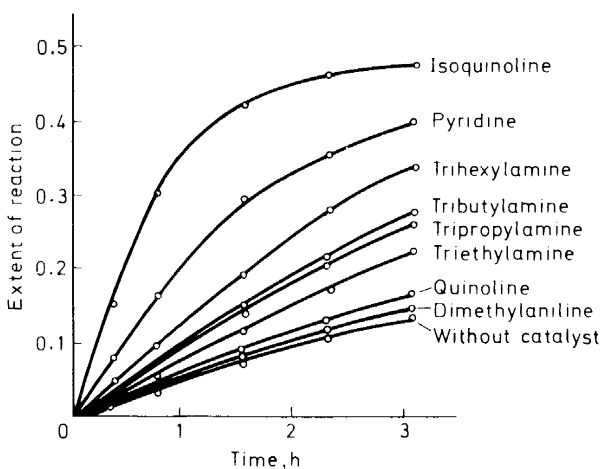


Figure 2. Polycyclotrimerization of 2,2-di-(4-cyanatophenyl)propane in the presence of tertiary amines (1 mol-%).

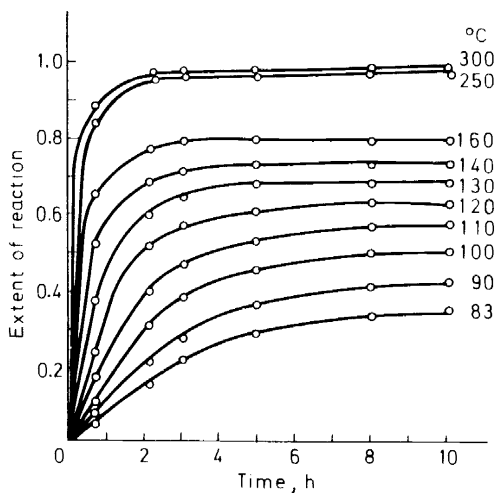
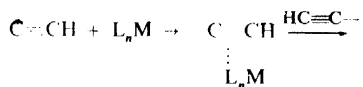
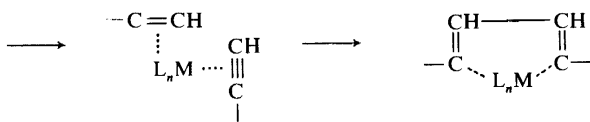


Figure 3. Polycyclotrimerization of 2,2-di-(4-cyanatophenyl)propane in the presence of  $ZnCl_2$  at various temperatures.

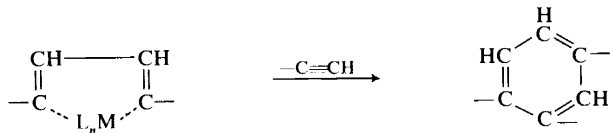
compound of the monomer with the catalyst is formed first, and then reaction with a second acetylene group takes place to give a cyclobutadiene ring<sup>26</sup>:



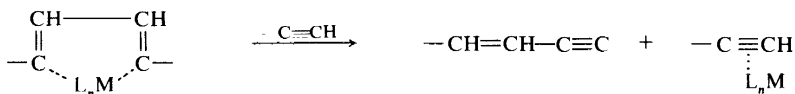
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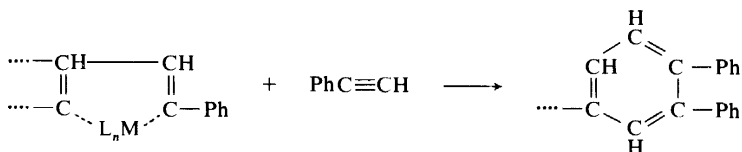
This intermediate compound reacts further with a third acetylenic bond:



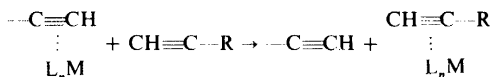
or else reacts with monomer to give a linear unit:



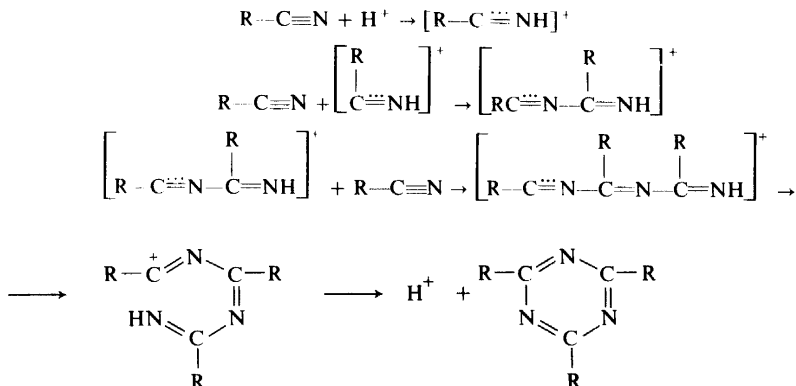
Termination can be accomplished in two ways. The first way consists of the reaction of the active unit with the monoacetylenic compound:



The second way consists of splitting-off the catalyst molecule and hence in inactivating the terminal multiple bond, as shown below:



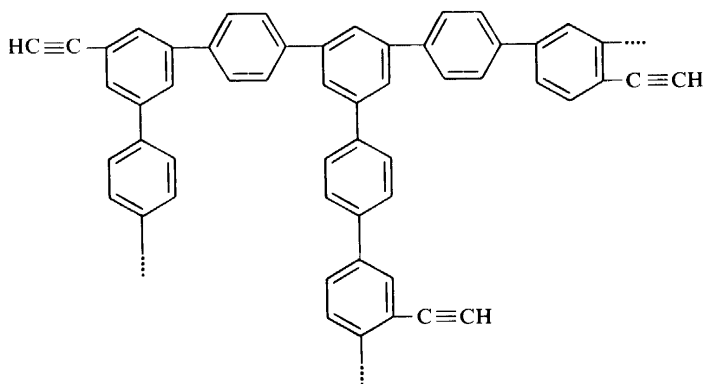
The mechanism of polycyclotrimerization of nitriles with an acidic catalyst can be represented as follows<sup>27</sup>:



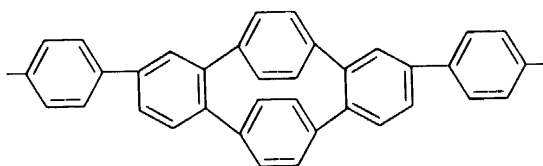




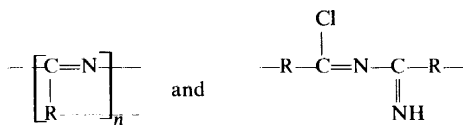
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On account of the residual triple bonds, such polymers may be cured by heating, becoming infusible and insoluble<sup>26</sup>. In addition to the structural features mentioned above, the resulting polymers can contain macrocycles of different size. Here is a scheme of such units:

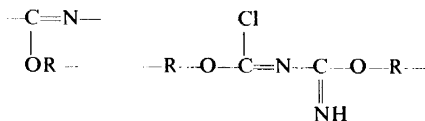


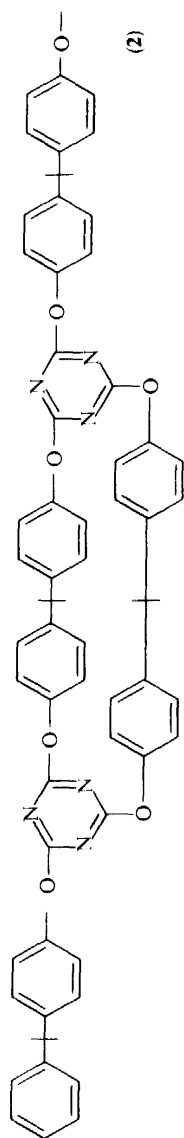
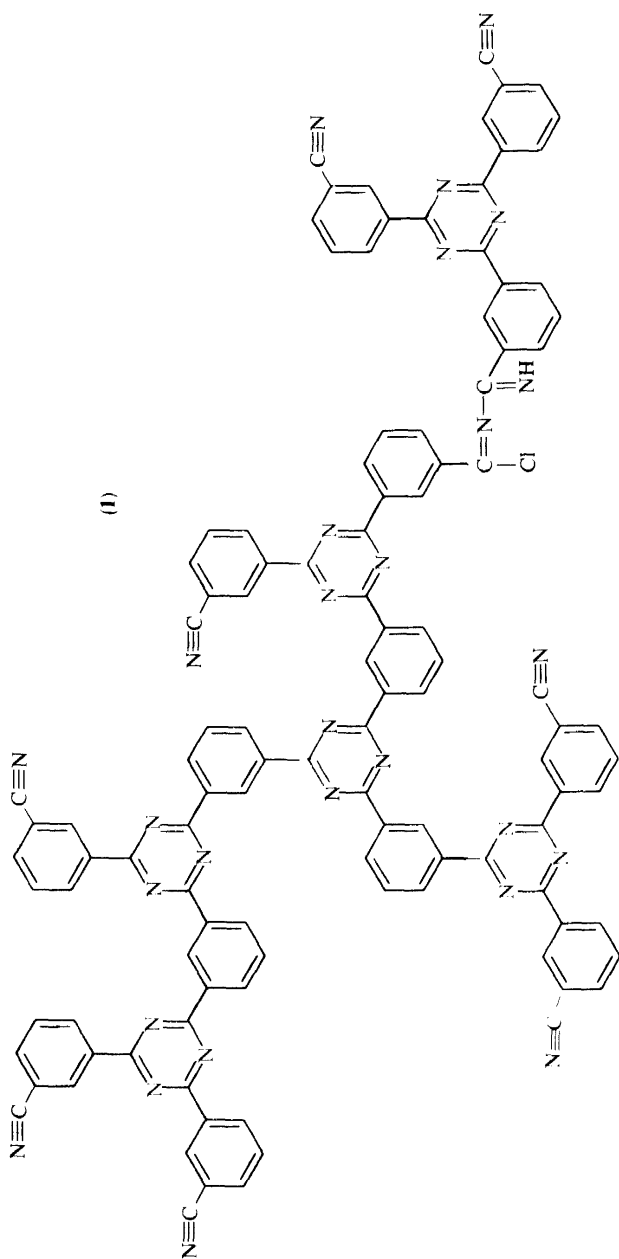
As in other cases of polycyclotrimerization, side-reactions take place leading to the formation of various cyclic and linear structures. Thus, the polycyclotrimerization of dinitriles yields a triazine ring and the following linear units:

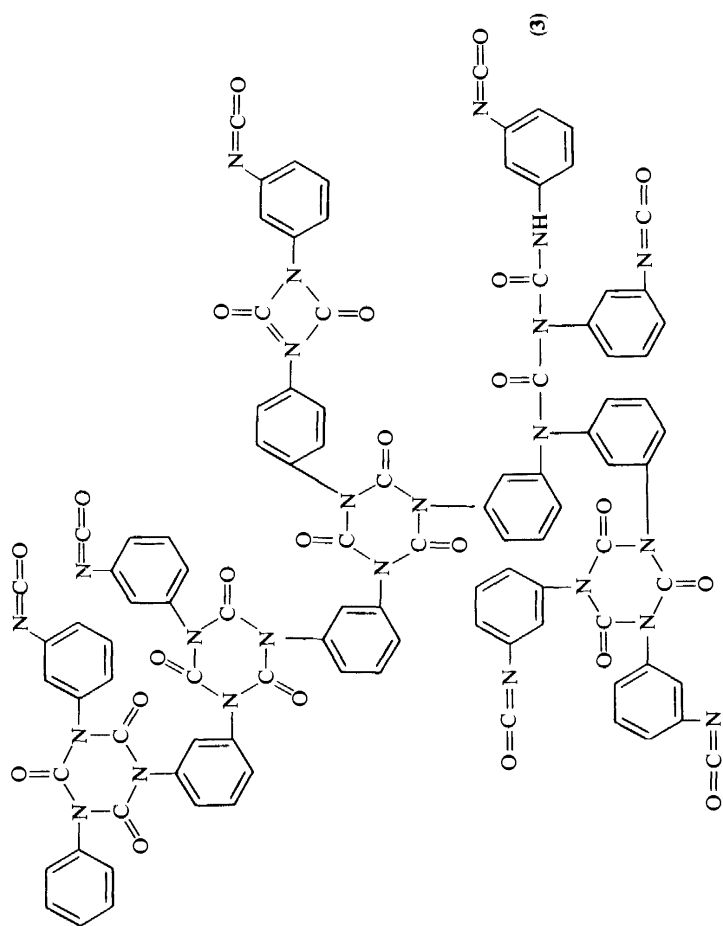


The structure of the polymer formed from the dinitrile of isophthalic acid can be illustrated schematically as shown at 1 overleaf<sup>27</sup>.

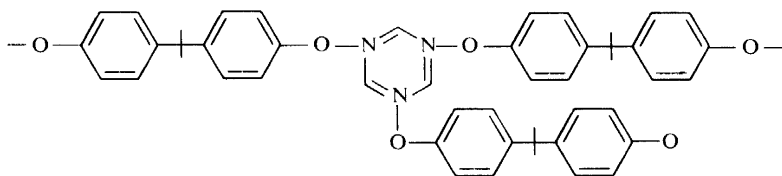
In this case, in addition to phenylene and triazine units, the polymer can contain nitrile groups and linear units which remain after the incomplete cyclotrimerization process. Cyanate cyclization can proceed similarly. Along with the six-membered ring of the cyanuric acid, the following linear units can be formed:



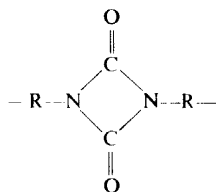




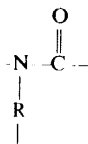
The structure of the resulting polymer in the case of bisphenol A cyanate can be represented as follows:



An investigation of the resulting polymers showed that they contain no appreciable structural irregularities. Their mechanical properties lead one to assume the presence of regular structures, consisting of macromolecules of different size bonded to each other, as shown schematically by formula 2. Cyclotrimerization of di-isocyanates proceeds in such a way that the isocyanurate rings predominate<sup>25</sup>. Cyclic dimers such as:

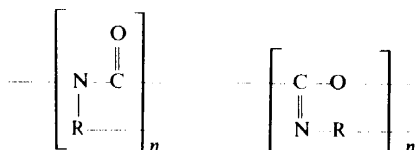


as well as the following linear structures are also possible:



Phosphine<sup>30</sup> and tertiary amine<sup>31</sup>, as well as sodium benzoate<sup>32</sup> and metal chelate-type<sup>6</sup> catalysts, favour the formation of the cyclic dimer. Also of importance is the structure of the di-isocyanate, since the aromatic di-isocyanurates are more readily dimerized than the aliphatic ones. The dimeric rings are less stable and more active than the trimeric rings.

In addition to the cyanurate rings, cationic catalysts can probably give rise to linear structures of the amide and ester type<sup>33</sup>:

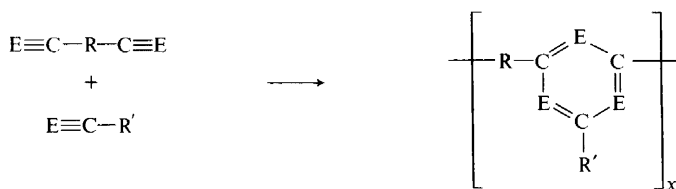


The structure of polymers formed by polycyclotrimerization of *m*-phenylene di-isocyanate can be represented as shown in formula 3.

## COPOLYMERS

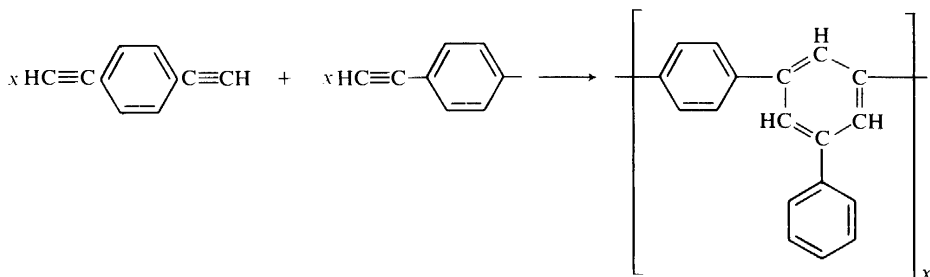
Formation of copolymers of diynic compounds with monoacetylenic monomers seems to be a rather effective method of preventing the formation of three-dimensional polymers, and which permits the preparation of soluble polymers and oligomers<sup>12, 34</sup>.

The corresponding monofunctional monomers were used as co-monomers. The copolymerization of mono- and di-acetylenes proceeds according to the scheme:



where E = N or C.

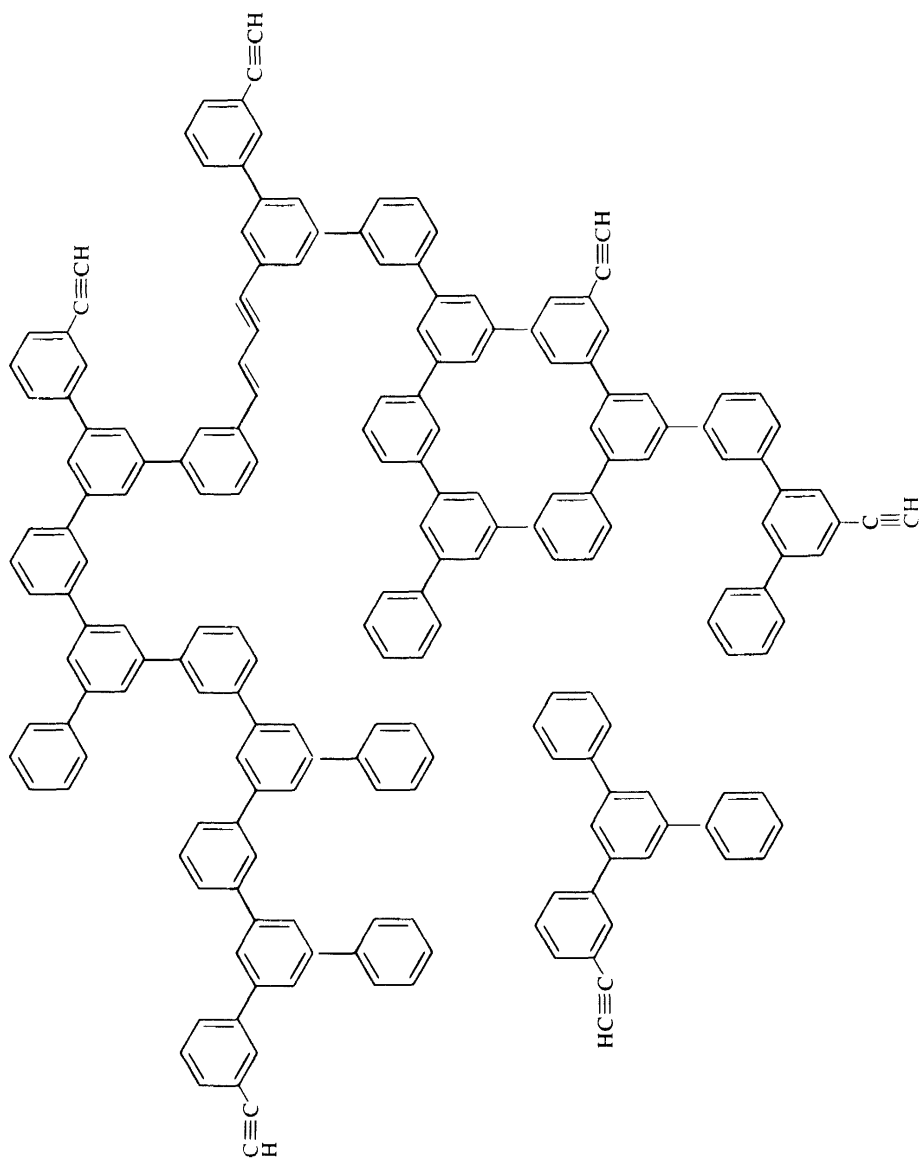
Phenylacetylene and its analogues and homologues were used as co-monomers in polycyclotrimerization of di-acetylenes. The amount of co-monomer required to prepare a fusible and soluble polymer depended upon its relative reactivity. The copolymerization of diethynylbenzene with phenylacetylene yielded a soluble copolymer at a monomer ratio 1 : 3<sup>12, 26, 35</sup>. The reaction may be described by the equation:



In this case a certain amount of the trimer is formed from the monofunctional compound. Phenylacetylene gives 1,2,4- and 1,3,5-triphenylbenzenes and probably *m*-bis(diphenylphenyl)benzene. The structure of such a copolymer of *m*-diethynylbenzene with phenylacetylene can be represented schematically:

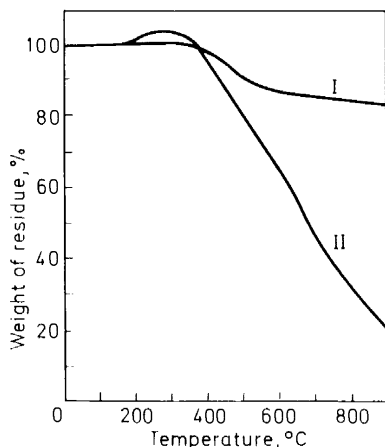
The presence of the residual triple bonds is responsible for the ability of such copolymers to be cured on heating; they become infusible and insoluble<sup>12, 26</sup>. But copolymers prepared with a large excess of phenylacetylene cannot be cured<sup>12</sup>.

In the case of dinitriles the mononitrile was used as comonomer, e.g. benzonitrile, which led to soluble polytriazines. In the case of dicyanates the monocyanate was added to give soluble polycyanurates.

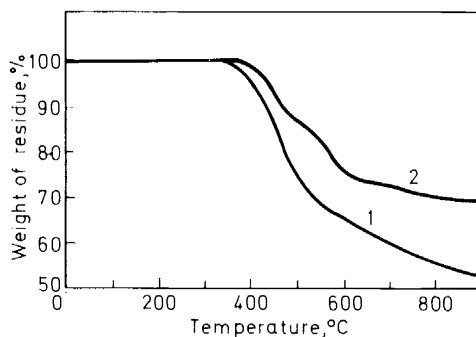


## PROPERTIES OF THE POLYMERS

An important characteristic of polycyclotrimerization is that in the resulting polymer the phenylene, triazine, cyanurate, or isocyanurate and other similar rings are formed. These rings are rigid, thermally stable structures, and the polymers are also characterized by high heat-stability<sup>36, 37</sup>. The polyphenylenes obtained by the copolycyclotrimerization of diacetylenes and monoacetylenes are, after curing, substances which begin to decompose only at temperatures above 400°C<sup>12, 14, 26</sup>. The TGA curves for such polymers are shown in *Figure 4*. The polytriazines prepared by polycyclotrimerization of dinitriles are also fairly thermally stable compounds<sup>27</sup>.



*Figure 4.* TGA curve for copolymer from diethynylbenzene and phenylacetylene (I - in helium; II - in air).



*Figure 5.* TGA of polycyanates from 4,4'-dicyanobiphenyl (1) and 9,9-di-(4-cyanatophenyl)-fluorene (2) in argon.

The polycyanurates formed by polycyclotrimerization of dicyanates are also of high thermal stability<sup>19</sup>, as can be seen from the TGA curves in *Figure 5*.

The polyisocyanurates obtained by polycyclotrimerization of di-isocyanates begin to decompose at 300°C.

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