U.D.C. 541.6:547.863.1

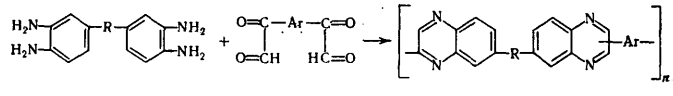
# Polyquinoxalines

A.M.Berlin

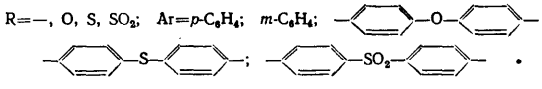
The present Review reports the most recent work on the synthesis, properties, and structure of a further class of thermostable heterocyclic polymers containing six-membered heterocyclic rings—the polyquinoxalines. A list of 24 references is given.

A considerable amount of research has been undertaken during recent years, both abroad and in the Soviet Union, on the production of thermostable polymeric materials. The fairly extensive class of macromolecular substances containing heterocyclic rings in the main chain is of undoubted interest, because several heterocycles, e.g. 1,3,5-triazine, oxadiazole, pyrazole, benzimidazole, benzoxazole, benzothiazole, etc., possess excellent stability to the action of heat, light, and oxidising agents, and are resistant to acids, bases, and various chemical reagents. The main investigations of the chemistry of macromolecular compounds containing five-membered heterocycles have been discussed in a number of reviews [1-4].

In view of the great thermal stability of the quinoxaline ring and its resistance to chemical reagents, several workers have synthesised polymers with chains containing these rings. They used the polycondensation of aromatic tetra-amines with bis-$\alpha$-diketones:



where

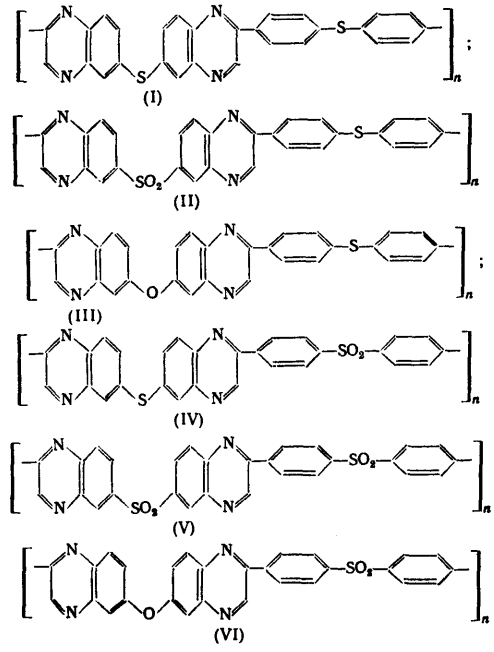


Two methods are at present used for the synthesis of polyquinoxalines: (1) stoichiometric quantities of the monomers are heated at 225–250°C for several hours [5], and the resulting polymer has an intermediate molecular weight which is then increased by further heating in a vacuum to 375°C; (2) the monomers first react in a solvent such as dioxan [5,6] or hexamethylphosphoramide (HMPA), [7] and the resulting solids of low molecular weight are again heated in a vacuum at 375°C. The polyquinoxaline obtained from *p*-phenylenediglyoxal and 3,3′-diaminobenzidine [5], which contains completely conjugated aromatic chains, possesses very high thermal stability when heated either in air or in nitrogen, its decomposition temperature being 500°C and above. It is insoluble in the usual organic solvents, and sparingly soluble in hexamethylphosphoramide; films obtained even from a polymer of high molecular weight are extremely brittle.

The introduction of an oxygen bridge into the polymer chain [8] increased the solubility of the polymers. Films cast from their solutions in hexamethylphosphoramide were also brittle initially, and showed various colours from pale yellow to red. After they had been heated in a vacuum in an atmosphere of nitrogen at 350–400°C, however, they were converted into tough, flexible, transparent films. Unfortunately, no information is given on the stability of these films. It is interesting that their infrared spectra have the same characteristic absorption bands before and after heating, which suggests the absence of cross-links in the polymer. On this basis the diminution in the solubility of the polymers after prolonged heating was explained by further increase in their molecular weight. This observation is common to all synthetic linear polyquinoxalines.

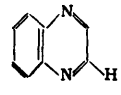
The presence of an oxygen bridge had no effect on the thermal stability of the polymers, the introduction of various sulphur-containing groups [9] produced only a slight decrease (the limit of thermal stability remained above 400°C even in air), and up to a considerable molecular weight these polymers retained their solubility not only in sulphuric acid but also in hexamethylphosphoramide (Table 1).

Polyquinoxalines [9] having the structures

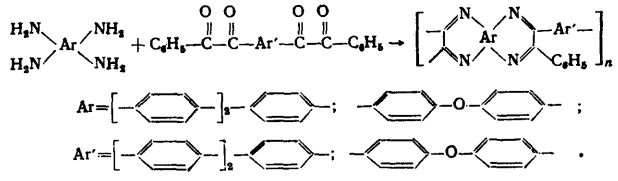


have been obtained.

It had been shown previously that the pyrazine hydrogen in the quinoxaline ring



undergoes oxidation first [10]. An attempt was therefore made [10] to increase the stability of polyquinoxalines to oxidation by replacing the pyrazine hydrogen by a phenyl group. Four phenylated polyquinoxalines were obtained by the scheme



These polymers were synthesised in the melt and in solution.

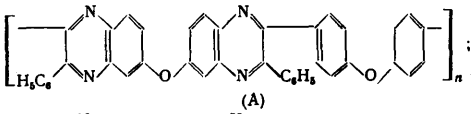
Condensation in the melt was performed at 180°, 200°, and 280°C and then at 380–400°C for 1 h. The resulting polymers exhibited extraordinarily good adhesion to glass. Various solvents—dimethylformamide, dimethylacetamide, *m*-cresol—were used for polycondensation in solution, between the temperature limits of −10° and 202°C. The initially formed polymer of intermediate molecular weight ($\eta = 0.6–1.0$) was then heated at 400°C until the final polymer ($\eta = 1.5–2.2$) was formed. Solutions of the polymers in *m*-cresol showed perfect stability for 30 days. Films from 10% *m*-cresol solutions of these polymers possessed a high tensile strength and excellent flexibility after being heated to 300°C.[10]

**Table 1.**

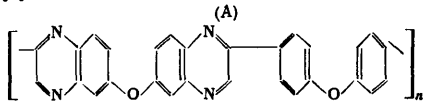
| Polymer | Stage | Colour | Solubility, % in HMPA | Solubility, % in $H_2SO_4$ | [η]* | Wt. lost at, °C |
|---|---|---|---|---|---|---|
| (I) | 1st | brown | 100 | 100 | 0.35 | — |
| | 2nd | black | 70 | 100 | 2.40 | 500 |
| (II) | 1st | yellow | 75 | 100 | 0.45 | — |
| | 2nd | brown | 55 | 90 | 0.80 | 440 |
| (III) | 1st | yellow | 100 | 100 | 0.35 | — |
| | 2nd | black | 19 | 70 | 1.07 | 460 |
| (IV) | 1st | brown | 100 | 100 | 0.41 | — |
| | 2nd | black | 50 | 80 | 1.12 | 460 |
| (V) | 1st | brown | 100 | 100 | 0.33 | — |
| | 2nd | brown | 21 | 80 | 1.22 | 420 |
| (VI) | 1st | yellow | 100 | 100 | 0.26 | — |
| | 2nd | black | 14 | 60 | 1.11 | 420 |

*[η] = logarithmic viscosity in hexamethylphosphoramide, concentration 0.25 g/100 ml.

Phenylated polyquinoxalines, as expected, exhibited outstanding thermal stability and resistance to oxidation. The authors showed this by making a thermogravimetric analysis (Fig. 1), and also by the isothermal aging (Fig. 2) in air and in helium of two polyquinoxalines differing only in the presence of phenyl groups in one of them.



(A)



(B)

In helium the difference between the temperatures at which decomposition begins in phenylated and ordinary linear polyquinoxalines is about 40 deg, and in air it is still larger. Furthermore, the phenylated polyquinoxalines have considerably higher glass points, the value for the polymer (A) being 437°C. It is interesting that both polymers (A) and (B) are stable in air at 316°C (600°F), and 92–95% of the original weight remains after heating for 200 h. However, after 100 h at 371°C (700°F) the polymer (A) retains 93% of the original weight, and polymer (B) only 63%; the latter breaks down completely after being heated for 160 h, whereas polymer (A) retains 50% of its weight after heating for 200 h (Fig. 2).

Phenylated polyquinoxalines are stable to the action of 40% alkali. After boiling in 40% caustic potash for 6 h, polymer (A) was regained in quantitative yield, its viscosity, analysis, and infrared spectra being unchanged.

The characteristics of several polyquinoxalines are given in Table 2.

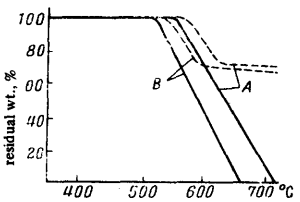
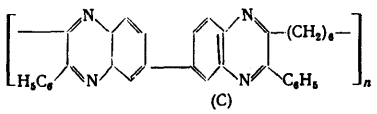
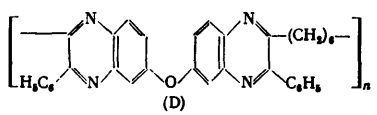



**Figure 1.** Thermogravimetric analysis of polyquinoxalines (A) and (B): full line in air; broken line in helium.

Aliphatic polyphenylquinoxalines have been obtained[11] by analogous methods to the above, by the reaction of 1,10-diphenyldecane-1,2,9,10-tetraone with 3,3′-diaminobenzidine or bis-3,4-diaminophenyl ether. As expected, the resulting polymers



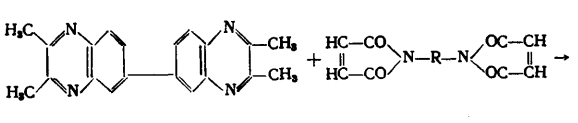
(C)

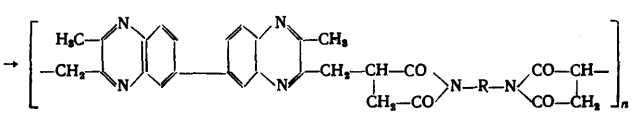


(D)

had a lower thermal stability than the aromatic polyphenylquinoxalines, their decomposition temperatures in air and in helium being about 450°C. The reduced viscosity (0.5% $H_2SO_4$ solution at 25°C) of such polymers was 1.16 and 1.04 for (C) and (D) respectively; they both possessed excellent adhesion to glass.

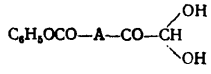
Quinoxalinimide polymers have been obtained[12] by the reaction of 2,2′,3,3′-tetramethylbiquinoxalinyl with *o*- and *m*-phenylenebismaleimides:



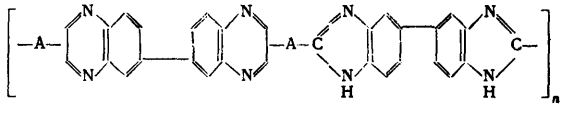


The reaction was conducted in anhydrous toluene, in xylene, or in dimethylformamide. The polymers are soluble in dimethylformamide, hexamethylphosphoramide, and sulphuric acid, do not melt, and lose 8% in weight when heated in air at 200°C for 2 h. No information is given on the molecular weight of the polymers.

New mixed polymers, polybenzimidazoquinoxalines, have been obtained[13] by the reaction of previously unreported phenoxycarbonylphenylglyoxals having the general formula



(where A represents *m*- or *p*-phenylene) with aromatic tetra-amines. In the opinion of the authors[13] quinoxaline rings are formed initially, and the structure of the resulting polymers corresponds to the formula



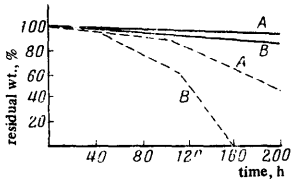
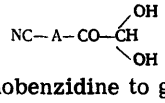


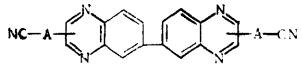

**Figure 2.** Kinetic curves for the loss in weight of polyquinoxalines (A) and (B) under isothermal conditions in air: full line at 316°C (600°F); broken line at 371°C (700°F).

The reduced viscosity of the polymers varied between 0.28 and 0.42.

Nitriles of glyoxals with the general formula



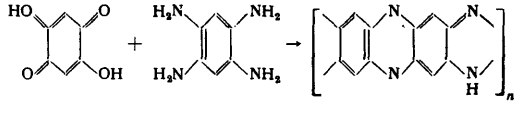
react with 3,3′-diaminobenzidine to give biscyanoarylbiquinoxalinyls



which in turn, on treatment with tetra-amine hydrochlorides in polyphosphoric acid, also formed polybenzimidazoquinoxalines.

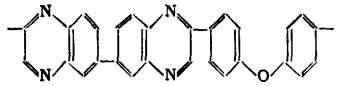
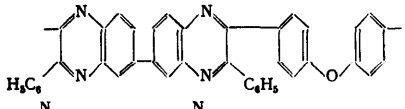
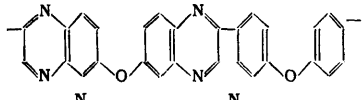
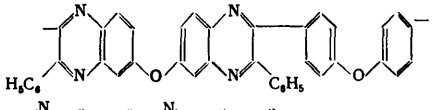
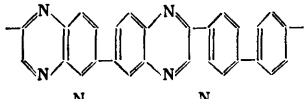
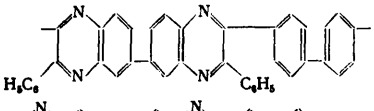
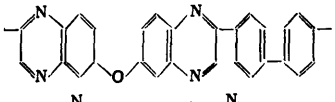
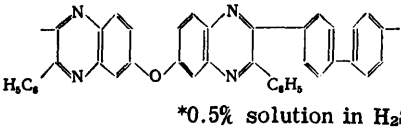
Published information indicates that work on the polyquinoxalines is developing in two main directions—(1) the synthesis of linear polyquinoxalines discussed above, and (2) the synthesis of ladderlike polyquinoxalines—the second line of research being further divided into two subgroups as it were—(*a*) substances such as tetra-amines and tetracarbonyl compounds are used for the synthesis, and (*b*) compounds already containing a quinoxaline ring are used.

The interaction of stoichiometric quantities of 2,5-dihydroxy-*p*-benzoquinone with the tetrahydrochloride of benzene-1,2,4,5-tetra-amine in dimethylacetamide, hexamethylphosphoramide, or polyphosphoric acid leads to the formation of a polymer having a ladderlike structure[14]:



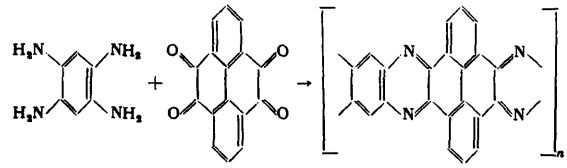
Polymers obtained in dimethylacetamide and hexamethylphosphoramide can be redissolved in these solvents after precipitation, and only after being heated at a low pressure do they lose their solubility. The occurrence of solubility in ladderlike polymers may be due to the formation of stable aggregates of polymer and solvent molecules, especially as ~ 20% of dimethylacetamide is removed from the polymer only by prolonged heating in a vacuum.

**Table 2.** Properties of polyquinoxalines[10].

| [Chain unit] | $\eta_{red}$*, dl g$^{-1}$ | Decomp. temp., °C, *in* air | Decomp. temp., °C, *in* He | Glass point | Residual wt. after heating in air at 371°C**, %, for 100 h | Residual wt. after heating in air at 371°C**, %, for 200 h |
|---|---|---|---|---|---|---|
|  | 2.06 | 510 | 530 | 388 | 60 | 0 |
|  | 2.05 | 520 | 550 | 420 | 80 | 40 |
|  | 1.61 | 510 | 540 | 382 | 70 | 0 |
|  | 2.16 | 550 | 560 | 437 | 93 | 50 |
|  | 1.42 | 530 | 540 | 386 | 70 | 0 |
|  | 1.50 | 530 | 550 | 404 | 90 | 45 |
|  | 1.75 | 520 | 540 | 390 | 64 | 0 |
|  | 1.71 | 530 | 550 | 410 | 78 | 35 |

*0.5% solution in $H_2SO_4$ at 25°C.
**Particle size 140–240 mesh.

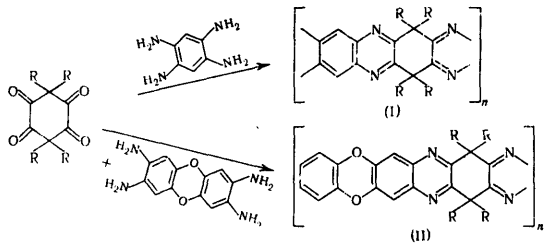
The thermal stability of these polymers in air was the same as that of the usual linear polyquinoxalines under similar conditions, probably owing to the presence in them of linear sections as well as the ladderlike structure. To test this hypothesis and obtain a completely aromatic ladderlike polyquinoxaline, pyrene-4,5,9,10-tetraone was used as the initial tetracarbonyl compound[15]:



These polymers dissolved in hexamethylphosphoramide and in hexafluoropropan-2-ol, which was rather unexpected for

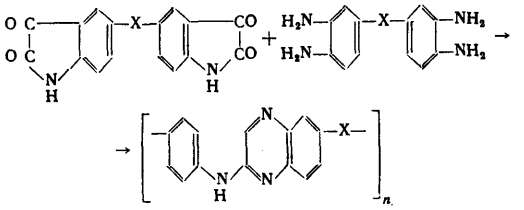
ladderlike polymers. They began to decompose in air at 460°C, and in nitrogen at 683°C, the losses in weight by the onset of decomposition being less than 4% in both cases. Thus it can be accepted that in this case the authors were able to obtain a completely aromatic ladderlike polyquinoxaline, which in an inert atmosphere surpassed in thermal stability the known linear aromatic polyquinoxalines.

As was to be expected, ladderlike polyquinoxalines ($\eta_{red}$ = 0.2–1.06) obtained from aliphatic tetracarbonyl monomers, e.g. 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetraone [16], are of no interest. Thermogravimetric analysis indicated that these polymers were considerably less stable than aromatic ladderlike polyquinoxalines: thus polymer (I) decomposes rapidly in air at 390°C, and (II) at 200°C.



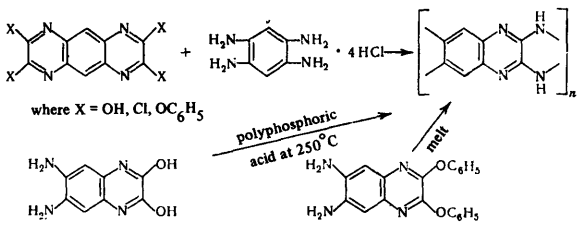
Both polymers begin to decompose slowly when heated in nitrogen at about 400°C.

Bulgarian scientists are investigating [17] the possibility of obtaining partly ladderlike polymers containing 6*H*-indolo[2,3-*b*]quinoxaline (indophenazine) as the main chain unit. Such polymers are prepared from the condensation of bisisatins with tetra-amines by heating in polyphosphoric acid:



They are powders, soluble in hexamethylphosphoramide, dimethylacetamide, dimethyl sulphoxide, and sulphuric acid. No data are given on their molecular weight or their thermal stability.

A ladderlike polymer has been obtained by condensing benzene-1,2,4,5-tetra-amine with a 2,3,6,7-tetrasubstituted 1,4,5,8-tetra-aza-anthracene [18,19] and by the self-condensation of 6,7-diamino-2,3-dihydroxy(or diphenoxy)quinoxaline:



Polycondensation was conducted in solution, in a melt, and in polyphosphoric acid; the reduced viscosity in methanesulphonic acid reached 2.5. Analogous polymers have been synthesised [19] also with 3,3′-diaminobenzidine. These polymers begin to lose weight when heated in air at about 350°C, and in nitrogen at 550°C, which is also explained by an imperfect ladderlike structure. This is evidently supplemented by too high a content of piperazine hydrogen atoms in the polymers, these being the first [10] to undergo thermo-oxidative degradation.

Thermally stable "ladderlike" or partly "ladderlike" polymers have recently been described which contain alternating quinoxaline and thiazine [20] or oxazine [21] units. They are obtained by condensing two diaminoarenedithiols—4,6-diaminobenzene-1,3-dithiol and 3,3′-dimercaptobenzidine—with three tetrachloro-derivatives of quinoxaline—2,3,6,7-tetrachloro-1,4,5,8-tetra-aza-anthracene, 2,2′,3,3′-tetrachloro-6,6′-biquinoxalinyl, and bis-2,3-dichloroquinoxalin-6-yl ether—in various combinations or by condensing diaminoarenediols, e.g. 2,5-diaminoquinol and 3,3′-dihydroxybenzidine, also with tetrasubstituted derivatives of quinoxaline. The solvents used for the reaction of aminoarenethiols are dimethylacetamide, hexamethylphosphoramide, and polyphosphoric acid. The resulting polymers are coloured powders, insoluble in the usual organic solvents and sparingly soluble in sulphuric and methanesulphonic acids. The reduced viscosity of a 0.2% solution of the polymers in methanesulphonic acid at 30°C varied from 0.22 to 1.55. A given polymer had a higher viscosity when dimethylacetamide was used as solvent in its preparation; polymers obtained in polyphosphoric acid had the lowest viscosities. No quinoxalinobenzoxazine was formed in dimethylacetamide; pyridine, naphthalene, and polyphosphoric acid were used as solvents to obtain the corresponding polymers.

Thermogravimetric analysis of polymers containing quinoxaline and thiazine units in the chain showed that in most cases they began to lose weight at about 500°C in nitrogen and at about 400°C in air. Data on thermal stability for the corresponding polymers containing oxazine rings are given only in an inert atmosphere, where they begin to lose weight at about 450°C.

The structure of polymers containing quinoxaline rings—both linear and "ladderlike"—was in all cases proved by a comparative study of the polymers and of model compounds, which included their ultraviolet spectra.

It is seen from the above survey that polyquinoxalines constitute an extremely promising class of thermostable polymers. Unfortunately, very little information is yet available on their practical application. It has been reported [22] that a plastic, which withstands heating to 480°C (900°F), has been developed on the basis of a polyquinoxaline of unstated composition. This material was tested at 590°C in an inert atmosphere, approaching the conditions of outer space. It is light, resembling graphite in structure, inelastic, and electrically non-conducting.

---o0o---

While this paper was being printed, further papers were published on the synthesis of ladderlike [23] and phenylated [24] polyquinoxalines.

## REFERENCES


1. C. S. Marvel, S. P. E. Journal, 20, 220 (1964).
2. Razvodovskii, Khim. Tekhnol. Polimerov, No. 12, 62 (1964).
3. F. T. Wallenberger, Angew. Chem. Internat. Edn., 3, 460 (1964).
4. A. A. Izyneev, M. M. Teplyakov, V. G. Samsonova, and A. D. Maksimov, Uspekhi Khim., 34, 2090 (1967) [Russ. Chem. Rev., No. 12 (1967)].
5. J. K. Stille and J. R. Williamson, J. Polymer Sci., B2, 209 (1964); A2, 3867 (1964).

6. G. P. Gaudemaris and B. J. Sillion, J. Polymer Sci., **B2**, 203 (1964).
7. J. K. Stille and F. E. Arnold, J. Polymer Sci., **A1**, 4, 551 (1966).
8. J. K. Stille, J. R. Williamson, and F. E. Arnold, J. Polymer Sci., **A3**, 1013 (1965).
9. J. K. Stille and F. E. Arnold, J. Polymer Sci., **A1**, 4, 551 (1966).
10. P. M. Hergenrother and H. H. Levine, J. Polymer Sci., **A1**, 5, 1453 (1967).
11. P. M. Hergenrother, J. Polymer Sci., **A1**, 6, 3170 (1968).
12. A. A. Berlin, T. V. Zelenetskaya, and R. M. Aseeva, Zhur. Vses. Khim. Obshch. Mendeleeva, **11**, 592 (1966).
13. B. Durif-Varambon, B. J. Sillion, and G. P. Gaudemaris, Compt. rend., **C-267**, 471 (1968).
14. J. K. Stille and E. L. Mainen, J. Polymer Sci., **B4**, 39 (1966).
15. J. K. Stille and E. L. Mainen, J. Polymer Sci., **B4**, 665 (1966).
16. J. K. Stille and M. E. Freeburger, J. Polymer Sci., **B5**, 989 (1967).
17. I. Shopov and N. Popov, Vysokomol. Soed., **9B**, 415 (1967).
18. F. Schryver and C. S. Marvel, J. Polymer Sci., **A1**, 5, 545 (1967).
19. H. Jadamus, F. Schryver, W. de Winter, and C. S. Marvel, J. Polymer Sci., **A1**, 4, 2831 (1966).
20. M. Okado and C. S. Marvel, J. Polymer Sci., **A1**, 6, 1259 (1968).
21. W. Rainer, M. Okado, and C. S. Marvel, J. Polymer Sci., **A1**, 6, 1503 (1968).
22. Electronic News, **9**, No. 429, 46 (1964).
23. J. K. Stille and E. Z. Mainen, Macromolecules, **1**, 36 (1968).
24. W. Wrasidlo and J. M. Augl, J. Polymer Sci., **B7**, 281 (1969).

Institute of Organoelementary Compounds, USSR Academy of Sciences, Moscow