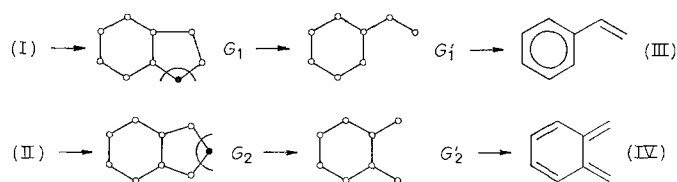


kind of vertices are marked (•) [3]. We present a graph-theoretical symbolism which should facilitate easy and practical systematization of any set of positional isomers. If a set of positional isomers is represented by graphs G_1, G_2, \dots, G_n and if vertices marked as • and belonging to the edges are removed, a set of partial graphs [6] G'_1, G'_2, \dots, G'_n of graphs G_i ($i = 1, 2, \dots, n$), which correspond to related hydrocarbons is obtained, e.g.:



Then we postulate that the topological factors which make (III) more stable (lower energy) than (IV) would favour (I) over (II). Some of these topology-dependent factors are given in our earlier work [7]. In the example presented above, the topological rule states that the quinonoid structure (IV) is more reactive than the delocalized structure (III), i.e. branching decreases the energy of conjugated systems (except in the case of 4-membered rings only, where a small energy gain is observed, compare (V) and (VI)) [7].



Thus, benzofuran (I) should be more stable than isobenzofuran (II), and consequently, they should differ in their structures and properties. This result is consistent with more rigorous quantum-mechanical calculations [8] and experimental findings [5].

We have studied various sets of positional isomers (containing one or more heteroatoms) and our results have always been compatible with experimental facts.

Received June 19, 1973

1. Visiting Professor from the Rugjer Bošković Institute, Zagreb
2. For review see Gutman, I., Trinajstić, N.: *Fortschr. Chem. Forsch.* **42**, 49 (1973)
3. Harary, F.: *Graph Theory*. Reading, Mass.: Addison-Wesley 1969
4. Trinajstić, N.: *Rec. Chem. Progr.* **32**, 85 (1971)
5. Warren, R. N.: *J. Amer. Chem. Soc.* **93**, 2346 (1971)
6. Graovac, A., *et al.*: *Theoret. Chim. Acta (Berlin)* **26**, 67 (1972)
7. Gutman, I., Trinajstić, N.: *Chem. Phys. Letters* **17**, 535 (1972)
8. Dewar, M. J. S., *et al.*: *Tetrahedron* **26**, 4505 (1970)

Autoradiography of Microgels

V. Neuhoff, D. I. Wolfrum and R. Röchel

Max-Planck-Institut für experimentelle Medizin,
Arbeitsgruppe Neurochemie, Göttingen, Germany

The autoradiography of polyacrylamide microgels prepared in capillaries [1] is of particular interest for recording, for example, the incorporation in or binding of radioactive substances to proteins. Placing the round, moist microgels on a sensitive X-ray film is unsatisfactory because of the small area of contact and because the gels dry out and shrink unevenly during exposure. Both drawbacks are eliminated by freeze-drying the microgels before autoradiography. The gels can be initially stained and evaluated microdensitometrically, after which they are transferred to a Petri dish containing about 2 mm of water, and the whole is frozen. The Petri dish is then placed on a second, precooled plate and the contents are lyophilized. The embedding in ice ensures that the gels retain their external form on freeze-drying and are therefore unable to shrink. If further stabilization of the gels during freeze-drying is desired, they can be embedded in a 2 mm layer of

0.5–1% agarose from which they are easily separated after drying. If no equipment for freeze-drying is available, the wet agarose layer can be wiped free of air bubbles with a wetted filter paper and the plate then dried in an oven at 37 °C. A faster method of drying is to hold the gels in soft tweezers and suspend them for a few minutes vertically in absolute ethanol. Complete dehydration requires approximately 30 min in abs. ethanol. During this procedure the gels shrink more or less evenly so that autoradiograms may be prepared.

If the gels are not already flat after drying, they may be pressed between two glass plates. They are then placed on a 3 × 3-cm glass plate and fixed to the plate with a drop of celloidin (1% in ether/ethanol 50:50). Finally the sensitive film from radiation-protection badges and a second glass plate are laid on the top in the darkroom, and the two plates fixed in position with adhesive tape. After exposure for a suitable length of time, the film is developed as usual. For the detection of very weak radioactivity, e.g. ³H radioactivity in faint protein bands, it may be advisable to use instead of the X-ray film the film-stripping technique on agarose-embedded gels. When dried gels are placed in acetic acid, they swell up and assume their original shape, and the previously stained bands appear unchanged. The gels can then be cut into slices and further evaluated by liquid scintillation counting. In the example shown in Fig. 1, human serum albumin preparation

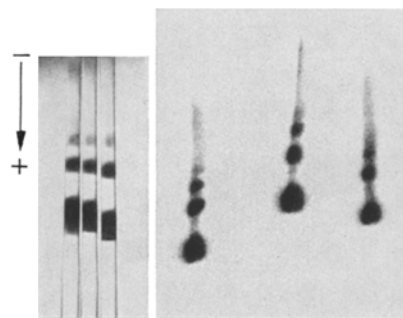


Fig. 1. On the right is the autoradiogram obtained from three freeze-dried 5 μ l microgels after fractionation and staining with amido black of a human albumin solution (on left) containing the monomer and three polymeric forms. The albumin solution was reacted with ¹⁴C-dansyl chloride prior to electrophoresis. Exposure time 8 h, magnification 3 ×

containing polymers as well as monomer was treated with ¹⁴C-dansyl chloride (specific activity 98 Ci/mole) and fractionated on 5 μ l polyacrylamide-gradient gels [2]. After staining with amido black, the gels were lyophilized and exposed to the X-ray film for 8 h. In addition to the intense blackening of the albumin monomer, 3 further bands of polymeric forms are clearly demonstrable.

Received July 5, 1973

1. Neuhoff, V.: *Micromethods in Molecular Biology (Molecular Biology, Biochemistry and Biophysics, Vol. 14. Eds. A. Kleinzeller, G. F. Springer, H. G. Wittmann)*. Berlin-Heidelberg-New York: Springer 1973
2. Röchel, R., *et al.*: submitted for publication

Zum Mechanismus der Substanzpolymerisation von Methacrylnitril

Klaus Marquardt und Peter Mehnert

Institut für Technische Chemie bzw.
Lehrstuhl für Verfahrenstechnik der TU München

Polymethacrylnitril (PMAN) ist in seinem Monomeren relativ schlecht löslich und fällt im Verlaufe der Polymerisation gelartig aus, so daß man die Polymerisation von Methacrylnitril zunächst weder eindeutig als heterogene noch als homogene Polymerisation bezeichnen kann [1, 2]. Die während der Polymerisation beobachtete Reaktionsbeschleunigung hielten Vance/Grassie [3] für den Effekt einer Verunreinigung, während Engel/Mehnert [4] feststellten, daß sie in Verbindung