

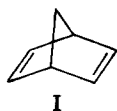
## Copolymerization Studies. IV. Transannular Copolymerization of Bicyclo[2.2.1]hepta-2,5-diene\*

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### Synopsis

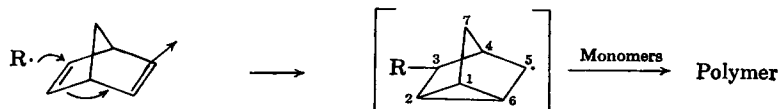
Bicyclo[2.2.1]hepta-2,5-diene, in the presence of free-radical initiators, homopolymerizes to a low molecular weight, soluble polymer containing both 3,5-disubstituted nortricyclene and 5,6-disubstituted bicyclo[2.2.1]hept-2-ene units in the polymer backbone. When the bicycloheptadiene ( $M_2$ ) is copolymerized with vinyl chloride, vinylidene chloride, acrylonitrile, ethyl acrylate, and methyl methacrylate, only the transannular product, 3,5-disubstituted nortricyclene, is found in the high molecular weight copolymers. Reactivity ratios for the above mentioned copolymerizations at 50°C. are:  $r_1 = 0.74$ ,  $r_2 = 0.35$ ;  $r_1 = 1.41$ ,  $r_2 = 0.08$ ;  $r_1 = 0.67$ ,  $r_2 = 0.08$ ;  $r_1 = 3.05$ ,  $r_2 = 0.01$ ;  $r_1 = 10.0$ ,  $r_2 = 0$ ; respectively. From these data, the  $Q$  and  $e$  values for bicyclo[2.2.1]hepta-2,5-diene average 0.09 and  $-1.04$ , respectively.

These investigations stem from two observations. The first was by Schmerling,<sup>2</sup> who noticed that small yields of low molecular weight, soluble, polymers were formed when bicyclo[2.2.1]hepta-2,5-diene (I) was warmed with a radical source. The second was in these laboratories when it was observed that under the mild homopolymerization conditions for bicycloheptadiene, bicyclo[2.2.1]hept-2-ene (II), was almost inert to reaction.



Since sterically there could not be enough difference between the monoolefin and the diolefin to allow facile polymerization through one double bond in the latter and not the former case, another propagation mechanism must have been in operation.

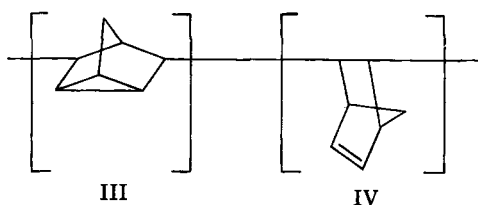
By analogy with free-radical reactions of bicycloheptadiene<sup>3</sup> it was thought that the homopolymerization could involve an intramolecular addition followed by an intermolecular addition, thus:



\* For Part III of this series, see Burkhart and Zutty.<sup>1</sup>

That just such a mechanism was in operation was easily seen from the infrared spectrum.

The appearance of a strong band at  $12.4\ \mu$  in the homopolymer absent in both bicycloheptene and bicycloheptadiene was indicative of the 3,5-disubstituted nortricyclene structure (III) in the polymer.<sup>4,5</sup> (The 3,6-disubstituted nortricyclene absorbs at  $11.7\ \mu$ .<sup>6</sup>) However, the strong band in the homopolymer at  $14.1\ \mu$  coupled with a band at  $6.4\ \mu$  also showed the presence of a cis-strained double bond. From such data poly(bicyclo[2.2.1]hepta-2,5-diene) is thought to be a more or less alternating copolymer containing both 3,5-disubstituted nortricyclene (III) and 5,6-disubstituted bicyclo[2.2.1]hept-2-ene (IV) (the structure obtained via addition through only one double bond in its backbone).



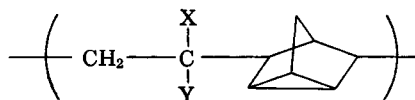
These data, along with the copolymerization data presented below, make it suspect that the formation of the nortricyclene structure is energetically more favorable than reaction through only one double bond but that steric requirements make it improbable for two nortricyclene units to be adjacent to each other.

It is interesting to note that the distance between the 2-6 and 3-5 carbon atoms in bicyclo[2.2.1]hepta-2,5-diene has been calculated<sup>7</sup> from electron diffraction data and found to be 2.37 Å., or about 1.6 times the normal carbon-carbon single bond distance in 1,3-butadiene.

Kargin<sup>8</sup> and co-workers have also studied this reaction, although at somewhat higher temperatures, and have indicated the structure of the resulting polymer to be solely that which is formed via polymerization through only one double bond of the bicyclohepta-2,5-diene (IV). Quite recently, however, Graham, Buhle, and Pappas<sup>9</sup> have noted that 2-carboxyethylbicyclo[2.2.1]hepta-2,5-diene homopolymerizes to a polymer containing structures due both to transannular addition, and reaction through only one double bond of the molecule.

Once the mechanism of the free radical-initiated homopolymerization of bicycloheptadiene became evident, attention was turned to copolymerization reactions. It was found that bicycloheptadiene copolymerized well, leading to high molecular weight, soluble polymers with acrylonitrile, ethyl acrylate, vinylidene chloride, vinyl chloride, and methyl methacrylate. Quite surprising was the fact that these copolymers contained very little, if any, unsaturation and had evidently formed via reaction of the bicycloheptadiene almost solely through the nortricyclene route. These data were again based upon infrared spectra which in all cases studied

showed almost the complete absence of the double bond bands at 6.4 and 14.1  $\mu$  and the appearance, when not masked by bands due to comonomer, of a strong band at 12.4  $\mu$  due to the 3,5-disubstituted nortricyclene. This was the case in all the copolymers reported below in the monomer-polymer composition curves in Figures 1-5. Thus it can be said that relatively easily attacked vinyl monomers and bicyclo[2.2.1]hepta-2,5-diene copolymerize to polymers having the following schematic structure:



The monomer-polymer composition curves for the above mentioned copolymerizations may be found in Figures 1-5. The monomer reactivity ratios ( $r_1$  and  $r_2$ ), calculated by the method of Fineman and Ross<sup>10</sup> from these data are shown in Table I. The  $Q$  and  $e$  values (based on styrene:  $Q = 1.0$ ,  $e = -0.8$ ) for bicyclo[2.2.1]hepta-2,5-diene calculated from these monomer reactivity ratios utilizing the best  $Q$  and  $e$  data available for vinyl chloride, vinylidene chloride, and acrylonitrile copolymerizations<sup>11</sup> are also shown.

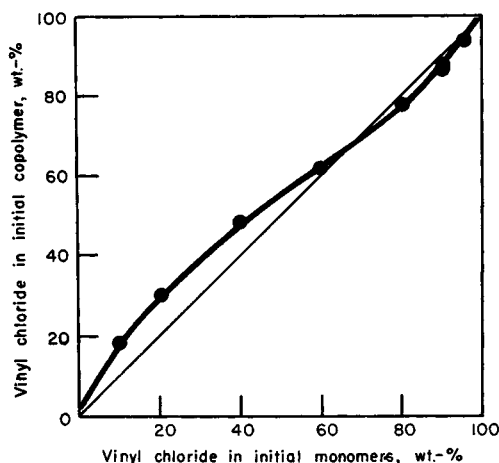


Fig. 1. Vinyl chloride-bicyclo[2.2.1]hepta-2,5-diene.

TABLE I  
Monomer Reactivity Ratios and  $Q$  and  $e$  Values for Bicyclo[2.2.1]hepta-2,5-diene  
Copolymerizations at 50°C.

$M_1$	$r_1$	$r_2$	$Q_2$	$e_2$
Vinyl chloride	0.74	0.35	0.06	-1.33
Vinylidene chloride	1.41	0.08	0.09	-1.19
Acrylonitrile	0.67	0.08	0.13	-0.60
Ethyl acrylate	3.05	0.01	—	—
Metnyl methacrylate	10.0	$\sim 0.00$	—	—

The  $r_1r_2$  product in all cases is considerably less than unity showing these copolymers to be quite alternating in nature, perhaps due, in part, to the steric requirements of the nortricyclene group. The low  $Q$  value for bicycloheptadiene shows bicycloheptadiene or intermediates to have

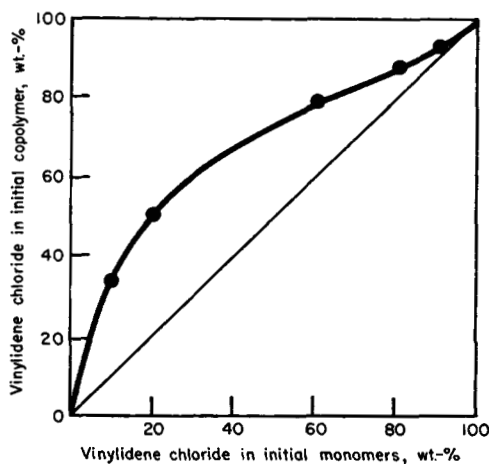


Fig. 2. Vinylidene chloride-bicyclo[2.2.1]hepta-2,5-diene.

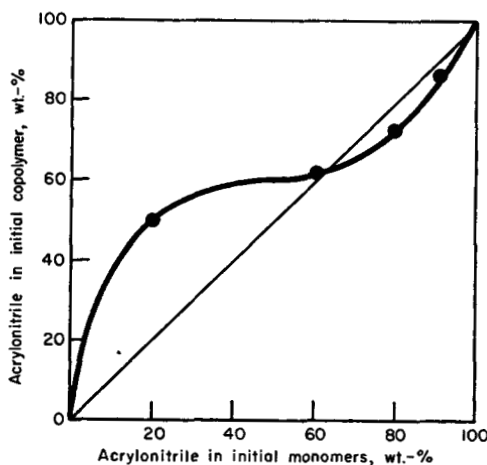


Fig. 3. Acrylonitrile-bicyclo[2.2.1]hepta-2,5-diene.

a fairly low degree of resonance stabilization while the high negative  $e$  value shows negative polarization of the radicals involved. These  $Q$ ,  $e$  values are similar to those for isobutylene ( $Q = 0.02$ ,  $e = -1.1$ ),<sup>12</sup> perhaps giving a clearer picture of the relative degrees of resonance stabilization and polarities encountered in the polymerization of bicycloheptadiene.

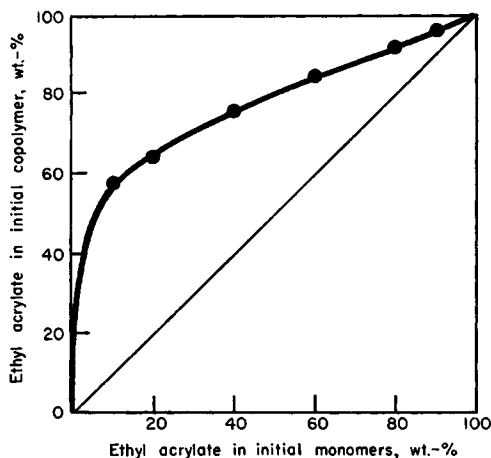


Fig. 4. Ethyl acrylate-bicyclo[2.2.1]hepta-2,5-diene.

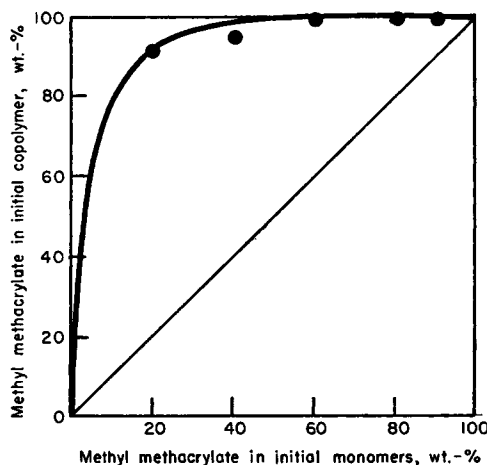


Fig. 5. Methyl methacrylate-bicyclo[2.2.1]hepta-2,5-diene.

### Experimental

All copolymerizations were run in crown-capped tubes rotating in a water-glycol bath at  $50 \pm 2^\circ\text{C}$ . The initiator was 0.2 wt.-% azobisisobutyronitrile. Most of the reactions were run in bulk, although several copolymerizations were carried out in 50% (v/v) benzene solution. Conversions were held to less than 10%. The copolymers formed were all of high molecular weight. Their reduced viscosities, measured at 0.2 wt.-% concentration in an appropriate solvent at  $30^\circ\text{C}$ ., were greater than 0.3. Copolymer compositions were determined by the appropriate elemental analyses. The bicyclo[2.2.1]hepta-2,5-diene (Shell Chemical Company) was carefully fractionated under pure nitrogen before use. Other monomers were freed from inhibitor by flash vacuum distillation and

center cuts retained for use. Polymerization rates varied depending on the comonomer pairs and their composition but usually were in the 0.5 to 5%/hr. range. Polymers were isolated by precipitation in methanol, washing with methanol and drying *in vacuo* at 55°C. Infrared spectra were run on either Baird or Perkin-Elmer double-beam instruments using a sodium chloride prism.

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### References

1. Burkhart, R. D., and N. L. Zutty, *J. Polymer Sci.*, **A1**, 1137 (1963).
2. Schmerling, L., U. S. Pat. 2,930,781 to Universal Oil Products (1960).
3. See, for example, S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).
4. Schmerling, L., *J. Am. Chem. Soc.*, **78**, 2819 (1956).
5. Roberts, J. D., *J. Am. Chem. Soc.*, **72**, 3116 (1950).
6. Kaplan, L., H. Kwart, and P. R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2342 (1960).
7. Wilcox, C. F., Jr., S. Winstein, and W. C. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).
8. Kargin, V. A., N. A. Plate, and L. A. Dudnik, *Vysokomol. Soedin.*, **1**, 420 (1959).
9. Graham, P. J., E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961).
10. Fineman, M., and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).
11. Thompson, B. R., and R. H. Raines, *J. Polymer Sci.*, **41**, 265 (1959).
12. Price, C. C., *J. Polymer Sci.*, **44**, 288 (1960).

### Résumé

Le bicyclo[2.2.1]hepta-2,5-diène homopolymérise en présence d'initiateurs par radicaux libres pour donner un polymère soluble de bas poids moléculaire qui contient dans la chaîne principale des unités de nortricyclène-3,5-disubstitué et de bicyclo[2.2.1]hept-2-ène-5,6-disubstitué. Lorsque le bicycloheptadiène ( $M_2$ ) est copolymérisé avec le chlorure de vinyle, le chlorure de vinylidène, l'acrylonitrile, l'acrylate d'éthyle et le méthacrylate de méthyle, on ne trouve, dans les copolymères de hauts poids moléculaire, que le produit transannulaire, le nortricyclène-3,5-disubstitué. Les rapports de réactivité des copolymérisations mentionnées ci-dessus, à 50°C. sont respectivement  $r_1 = 0.74$ ,  $r_2 = 0.35$ ;  $r_1 = 1.41$ ,  $r_2 = 0.08$ ;  $r_1 = 0.67$ ,  $r_2 = 0.08$ ;  $r_1 = 3.05$ ,  $r_2 = 0.01$ ;  $r_1 = 10.0$ ,  $r_2 = 0$ . En utilisant ces données et les valeurs de  $Q$  et de  $e$ , on obtient pour le bicyclo[2.2.1]hepta-2,5-diène respectivement 0.09 et  $-1.04$ .

### Zusammenfassung

Bicyclo[2.2.1]hepta-2,5-dien polymerisiert in Gegenwart radikalischer Starter zu einem niedermolekularen, löslichen Polymeren, das in der Hauptkette 3,5-disubstituierte Nortricyclen- und 5,6-disubstituierte Bicyclo[2.2.1]hept-2-en-einheiten enthält. Bei Copolymerisation des Bicycloheptadiens ( $M_2$ ) mit Vinylchlorid, Vinylidenchlorid, Acrylnitril, Äthylacrylat und Methylmethacrylat tritt in den hochmolekularen Copolymeren nur das transannulare Produkt, 3,5-disubstituiertes Nortricyclen, auf. Die Reaktivitätsverhältnisse für die Copolymerisationen in der oben angegebenen Reihenfolge sind bei 50°C.:  $r_1 = 0.74$ ,  $r_2 = 0.35$ ;  $r_1 = 1.41$ ,  $r_2 = 0.08$ ;  $r_1 = 0.67$ ,  $r_2 = 0.08$ ;  $r_1 = 3.05$ ,  $r_2 = 0.01$ ;  $r_1 = 10.0$ ,  $r_2 = 0$ . Aus diesen Zahlen ergeben sich die  $Q$ - und  $e$ -Werte für Bicyclo[2.2.1]hepta-2,5-dien in Mittel zu 0.09 bzw.  $-1.04$ .

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