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The Polymerization of Some Bulky Spirooxetanes

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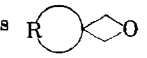
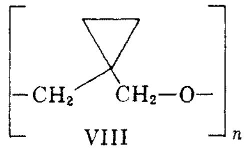
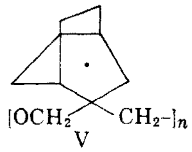
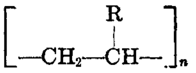
A series of spirooxetanes  has been prepared, in which the hydrocarbon group R has been varied widely in terms of its bulk. The oxetanes polymerized readily to polymers in which the crystalline melting point varied from 45° (VIII) to 290° (V). The increase in crystalline melting point can be related directly to increase in bulk of the lateral group,


VIII


V

just as in the case of the isotactic polyhydrocarbons,

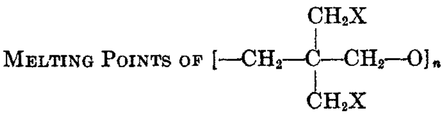

$$\left[-CH_2-\overset{R}{\overset{|}{C}}H-\right]_n$$

It has long been considered that the introduction of a nonpolar lateral group on a polymer chain would have the effect of decreasing crystallinity and melting point by interfering with the ability of chains to line up and crystallize.[1] Evidence to the contrary became very apparent in the isotactic polyhydrocarbon system, where lateral alkyl groups raised the melting point, to a degree related to the bulk of the alkyl group[2] without interfering with crystallizability. Examination of the literature showed other cases, such as the alkylbutadienes,[3] where similar effects were noted.

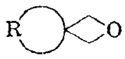
In the case of polyethers derived from oxetanes, it has been observed that halomethyl groups have a strong effect on the melting point. Thus, the polymer from 3,3-dimethyloxetane has a crystalline melting point of 47°,[4] while that from bis(chloromethyl)oxetane melts at 180°.[5] This increase may be attributable to a combination of bulk[6] and presence of a polar substituent.

In order to study steric effects caused by lateral bulky groups on the melting of polyethers of this type, synthesis and polymerization of a series of spirooxetanes, in which the bulkiness was introduced solely in the form of hydrocarbon residues, was undertaken. The spiro configuration eliminates rotational influences in the side chain and provides a monomer which must polymerize to a unique linear structure, that is, a polymer in which rings are rigidly fused perpendicular to the chain, like the blades of a fan.

TABLE I

MELTING POINTS OF 
$$\left[-CH_2-\underset{CH_2X}{\overset{CH_2X}{C}}-CH_2-O\right]_n$$

X	M.P.	Ref.
H	47	4
F	135	7
Cl	180	5, 8
Br	220	8
I	290	8



Synthesis of monomers. Acrolein was condensed with a series of conjugated dienes to give the corresponding aldehydes, which were then condensed with formaldehyde to give 1,3-glycols. The glycols were converted to ditoluenesulfonates, which were then fused with alkali to give the oxetanes. The synthesis of 2-oxaspiro[3.5]nonane[9] is shown in the flow diagram, and represents a typical synthesis.

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(1) R. Hill, Ed., *Fibres from Synthetic Polymers*, Elsevier, Amsterdam, 1953; see p. 319 *ff*.

(2) T. W. Campbell and A. C. Haven, *J. Applied Polymer Sci.*, **1**, 73 (1959).

(3) C. G. Overberger, L. A. Arond, R. H. Wiley, and R. R. Carrett, *J. Polymer Sci.*, **7**, 431 (1951). Other examples are summarized in ref. 2.

(4) J. B. Rose, *J. Chem. Soc.*, 542, 546 (1956).

(5)(a) A. C. Farthing and W. J. Reynolds, *J. Polymer Sci.*, **12**, 503 (1954). (b) A. C. Farthing, *J. Chem. Soc.*, 3648 (1955).

(6) Note that the polymer from the very bulky bis(phenoxymethyl)oxetane is amorphous[5b] and has a low softening point.

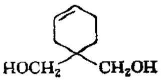
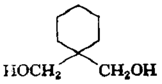
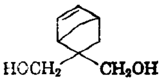
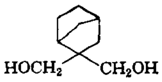
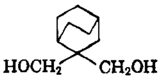
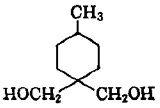
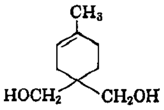
(7) Y. Etienne, *Ind. des Plastiques Modernes*, **9**, 37 (1957).

(8) T. W. Campbell, *J. Org. Chem.*, **22**, 1029 (1957).

(9)(a) S. Searles, R. N. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959). (b) E. L. Wittbecker, H. K. Hall, Jr., and Tod W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960).

TABLE II

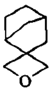
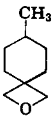
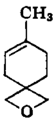
PREPARATION OF 1,3-DIOLS FROM ALICYCLIC ALDEHYDES

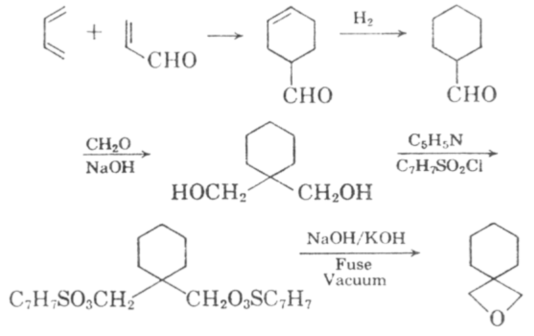
						Tosylates			
Diol	M.P.	Empirical Formula	Calcd., %	Found, %	Yield, %	M.P.	Empirical formula	Calcd., %	Found, %
	94.5–95.0	$C_8H_{14}O_2$	C: 67.6 H: 9.9	67.4 67.2 10.1 10.2	92	75.5–76.5	$C_{22}H_{26}O_6S_2$	C: 58.63 H: 5.82	58.79 58.58 5.90 5.87
	99.0–99.5	$C_8H_{16}O_2$	—	—	86[a]	90–91	$C_{22}H_{28}O_6S_2$	C: 58.40 H: 6.19	58.7 58.6 6.4 6.5
	114.5–115.0	$C_9H_{14}O_2$	C: 70.10 H: 9.14	69.88 69.97 9.19 9.20	76	129.0–129.5	$C_{23}H_{26}O_6S_2$	C: 59.76 H: 5.68	59.8 60.0 6.04 6.06
	98.0–99.0	$C_9H_{16}O_2$	C: 69.20 H: 10.30	69.36 69.39 10.50 10.55	69[a]	107–108	$C_{23}H_{28}O_6S_2$	C: 59.50 H: 6.08	59.54 59.62 6.34 6.35
	131.0	$C_{10}H_{18}O_2$	C: 70.56 H: 10.50	70.4 70.7 10.61 10.66	66[b]	114.5–116.0	$C_{24}H_{30}O_6S_2$	C: 60.23 H: 6.32	60.0 60.2 6.5 6.6
	86–96	$C_9H_{18}O_2$	C: 68.3 H: 11.3	68.7 68.7 10.8 11.1	10	72.5–74	$C_{23}H_{30}O_6S_2$	C: 59.23 H: 6.43	59.31 59.27 6.36 6.47
	113–113.5	$C_9H_{16}O_2$	C: 69.2 H: 10.25	69.7 69.9 11.00 11.06	41	99–100	$C_{23}H_{28}O_6S_2$	C: 59.5 H: 6.0	59.6 59.4 6.2 6.1

[a] Based on tetrahydrobenzaldehyde (2 steps). [b] Based on cyclohexadiene (3 steps).

TABLE III

PREPARATION OF OXETANES FROM DITOSYLATES

Oxetane	B.P.	Empirical Formula	Calcd., %	Found, %	Yield, %
	178/760 mm. 74/20 mm.	$C_8H_{12}O$	C: 77.36 H: 9.74	76.8 76.9 9.6 9.7	54
	64/14 mm.	$C_8H_{14}O$	C: 76.13 H: 11.18	75.95 76.01 11.11 11.03	45
	81/20 mm.	$C_9H_{12}O$	C: 79.37 H: 8.89	79.12 78.97 9.01 8.94	28
	90–91/24 mm.	$C_9H_{14}O$	C: 78.22 H: 10.21	78.02 78.07 10.01 9.96	33
	117/24 mm. (m.p. 36°)	$C_{10}H_{16}O$	C: 78.91 H: 10.59	78.8 78.6 10.8 10.7	19
	120–21/81 mm.	$C_9H_{16}O$	C: 77.2 H: 11.4	77.2 77.4 11.0 11.0	10
	74–75/11 mm.	$C_9H_{14}O$	C: 78.3 H: 10.1	78.0 78.0 10.0 9.9	13

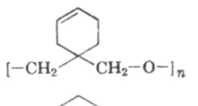
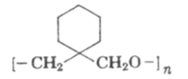
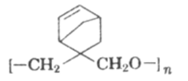
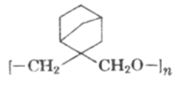
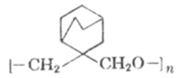
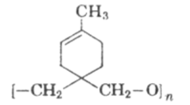
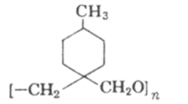
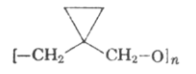


Physical properties of the glycols and ditosylates are summarized in Table II. Data for the oxetanes are shown in Table III.

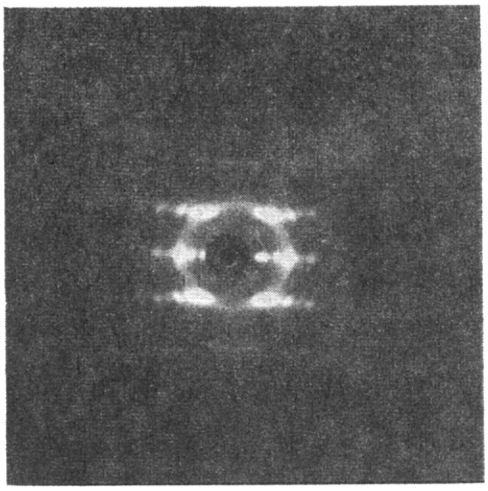
Polymerization of oxetanes. The monomers shown in Table III all polymerized readily with phosphorus pentafluoride catalyst in refluxing methyl chloride (−25°) as solvent.[8,9b,10] Successive extraction of polymers with ether and alcohol gave only a small amount of amorphous low molecular weight polymer and no crystalline oligomers.[4] The polyethers were *all highly crystalline* despite the extremely bulky groups present. Films from I were rubbery when pressed, but could be crystallized in boiling acetone, as could the other polymers.

TABLE IV

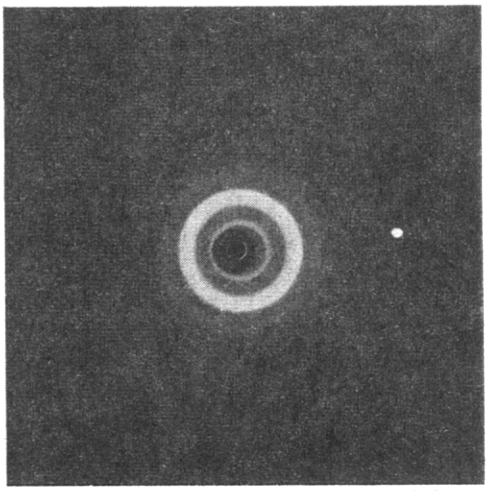
Preparation of Polyethers from Spirooxetanes

Polymer	Cryst. M.P.	Empirical Formula	Calcd., %	Found, %
	102	$(C_8H_{12}O)_n$	C: 77.36 H: 9.74	77.2 76.9 10.05 9.91
	152	$(C_8H_{14}O)_n$	C: 76.13 H: 11.18	76.1 76.2 10.6 10.7
	190	$(C_9H_{12}O)_n$	C: 79.37 H: 8.89	79.8 79.6 9.4 9.1
	208	$(C_9H_{14}O)_n$	C: 78.22 H: 10.21	78.0 77.9 10.49 10.52
	290	$(C_{10}H_{16}O)_n$	C: 78.91 H: 10.59	78.1 78.3 11.0 11.1
	155	$(C_9H_{14}O)_n$	—	—
	165	$(C_9H_{16}O)_n$	C: 77.2 H: 11.4	77.3 11.0
	45	$(C_5H_8O)_n$	—	—

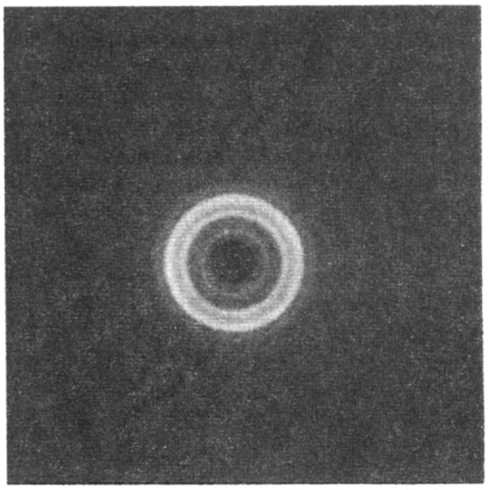
(10(a) T. W. Campbell, U. S. Patent 2,831,825, April 22, 1958, and 2,891,837, June 23, 1959. (b) E. L. Muetterties, U. S. Patent 2,856,370, Oct. 14, 1958.



Polymer I, stretched 4× and crystallized



Polymer II, melt-pressed and annealed



Polymer IX, cast from chloroform solution

Fig. 1. X-ray patterns of polymers from spirooxetanes

Examples of x-ray patterns will be found in Fig. 1. The fiber diagram for polymer I is extremely complicated and shows a high degree of order.

Not all the polyethers were prepared in high enough molecular weight to be classified as tough;

however, all could be pressed to clear, coherent films, on which crystalline melting points could be determined. Data on the polymers are collected in Table IV.

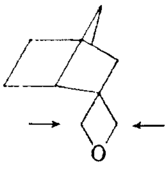
For comparative purposes, 2-oxaspirohexane

was synthesized[11] and polymerized to a linear polyether with planar cyclopropane rings fused to the polymeric chain. This melted at about the same temperature as the polyether from 3,3-dimethyloxetane.

In addition, a copolymer of bis(chloromethyl)oxetane and 2-oxaspiro[3.5]nonene-6 (17:1) was prepared, which had properties similar to those of the homopolymer from bis(chloromethyl)oxetane,[5,8] but which could be subsequently cross-linked (cured) to an intractable solid.

DISCUSSION

As expected, the crystalline melting points of the various polymers could all be related to the bulk of the appended R group (Table IV). Polymer VIII (cyclopropane side group) has a planar ring attached, with little opportunity for interaction of successive rings. Going to six carbons, however, gives a ring which can pucker, hence is effectively thicker and more likely to contact its neighbors. Polymer II melts at 152°, over 100° higher than VIII. Introducing a double bond in the six-membered ring flattens it somewhat, and drops the melting point of the polymer (I) to 102°. In the bridged systems III, IV, and V, the lateral groups approach a spherical state and afford greatly increased bulk and opportunity for interaction; hence this series has the highest melting points. However, it should be realized that all polymers except II and VII may actually be copolymers, since attack of the growing chain can occur at either side of the oxetane ring, to give two different configurations of the lateral group, for example:



The very high *crystalline* melting points of these copolymers is strong evidence for the importance of the bulk factor.

In polymers VI and VII, a methyl group has been introduced in the 4-position. In VI, the methyl group is planar and apparently is sufficiently effective to counteract the introduction of the double bond (compare with I and II). In VII, the methyl group is no longer planar, hence the copolymer effect accounts for the relatively modest increase in melting point over VI.

The x-ray patterns of these polymers (Fig. 1) are quite complex, showing high crystallinity and regularity of structure. Examination of a portion of the chain constructed from Stuart-Briegleb models reveals that there are several very regular configurations that the chain can assume. A "spiral staircase" arrangement appears most probable. X-ray patterns are being analyzed, and the structure of the unit cell will be the subject of a separate communication.

EXPERIMENTAL

All melting points were taken on Kofler hot stage.

Preparation of aldehydes. The unsaturated aldehydes required were prepared by a Diels-Alder condensation of acrolein with the appropriate diene. The saturated aldehydes were prepared by hydrogenation of the corresponding unsaturate over 5% palladium on charcoal. Most of the compounds are described in the literature: Δ^3-tetrahydrobenzaldehyde,[12] hexahydrobenzaldehyde,[12] endo-2,5-methano-Δ^3-tetrahydrobenzaldehyde[12], endo-2,5-methanohexahydrobenzaldehyde,[12,13] endo-2,5-ethanohexahydrobenzaldehyde,[13] 4-methyl-Δ-^{3}-tetrahydrobenzaldehyde,[14] 4-methylhexahydrobenzaldehyde.[14,15]

Conversion of aldehydes to 1,3-glycols. This was done by condensation with formaldehyde in strong alkali.[16,17,18] The following typical procedure was used.

In a 5-l., three-neck flask equipped with a stirrer, a condenser, and a dropping funnel were placed 4.0 moles of the appropriate aldehyde and 1000 g. of 37% aqueous formaldehyde solution. To this mixture cooled externally with ice was added slowly from a dropping funnel 390 g. of solid potassium hydroxide dissolved in about 2400 ml. of absolute ethanol. The original two-phase system shortly became homogeneous and a mild exothermic reaction was observed. The alcoholic alkali was added at such a rate that the temperature did not exceed 50–60°. When the alkali was all added, the mixture was allowed to stir for 2-3 hr. and then most of the alcohol was removed by distillation. The residual two-phase system consisting of strong aqueous alkali and the product was poured into an enamel pan and allowed to cool. The desired product crystallized and was separated from the strong alkaline solution by vacuum filtration. The solid was sucked as dry as possible and allowed to dry in air. The crude diol containing a fair amount of sodium carbonate was now recrystallized from benzene using approximately 200 ml. of benzene for every 100 g. of diol. The hot benzene solution was treated with decolorizing carbon, filtered and cooled. The pure diol was obtained in essentially quantitative recovery. Properties are listed in Table II.

The diols were converted to ditosylates with toluene sulfonyl chloride in pyridine-chloroform. The ditosylates were used directly in the preparation of oxetanes. Analytical samples were recrystallized from isopropanol. Data are shown in Table II.

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(11) S. Searles and E. Lutz, *J. Am. Chem. Soc.*, **81**, 3674 (1959).

(12) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(13) O. Diels and K. Alder, *Ann.*, **478**, 137 (1930).

(14) O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

(15) K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

(16) H. Bruson, W. D. Niederhauser, and H. Iserson, U. S. 2,417,100 (March 11, 1947).

(17) H. Bruson and W. D. Niederhauser, U. S. 2,418,290 (April 1, 1947).

(18) H. E. French and D. M. Gallagher, *J. Am. Chem. Soc.*, **64**, 1497 (1942).

Preparation of oxetanes. General method. Potassium and sodium hydroxide were powdered and a mixture of equal weights of the two was prepared. For preparation of the oxetane, one part of the ditosylate was intimately mixed with two to three parts of the potassium–sodium hydroxide mixture and placed in a round bottom, single-neck flask of adequate capacity. (Some swelling of the mixture occurs on heating.) The mixture of materials was heated in a high vacuum to a temperature of 300–400°. The gaseous products were trapped in a Dry Ice–cooled flask followed by a Dry Ice–cooled trap. When no more material appeared to be coming out of the frothing mixture, the distillation was stopped and the traps were allowed to warm to room temperature. A mixture of two liquids was obtained, the bottom layer consisting of water and the top layer consisting of the desired organic material contaminated with by-products. The organic layer was separated, washed with water, and dried, then distilled through a spinning band column. Properties of the oxetanes are shown in Table III. These oxetanes are shown in Table III. These oxetanes are rather prone to autoxidation and should be protected from oxygen. All of them showed the characteristic oxetane infrared band at *ca.* 10.2 μ.[8]

Polymerization of oxetanes. General method. Two to five grams of pure monomer was placed in a 100-ml., three-necked flask equipped with a stirrer, a gas inlet, and a Dry Ice condenser, and maintained under an atmosphere of nitrogen. From a cylinder about 50 ml. of methyl chloride was condensed into the flask which was cooled in a Dry Ice bath. The methyl chloride cylinder was detached and the contents of the flask stirred and refluxed (−25°) gently. To the reaction vessel was now connected a small tube containing 1–2 g. of *p*-chlorobenzenediazonium hexafluorophosphate[19] by means of a short length of tubing. A stream of nitrogen was passed through the tube containing the diazonium salt into the reaction vessel. The diazonium salt was heated in an oil bath to about 150°–160° to cause evolution of phosphorus pentafluoride, which was swept with the nitrogen stream into the reaction vessel. Polymerization of the oxetane usually occurred within a very short time if the monomer was of a high degree of purity. The polymer separated from the methyl chloride either as a white powder or as a swollen mass similar in appearance to cottage cheese. The polymerization was exothermic and vigorous boiling of the methyl chloride occurred. After a few minutes a small amount of methyl alcohol was added to inactivate the catalyst. The methyl chloride was allowed to evaporate, and the solid residue consisting of polyether was separated, washed, and dried. Polymers were extracted with ether and alcohol, to remove traces of low molecular weight materials. No crystalline oligomers could be detected. The yield was usually quantitative. In all cases studied it was possible to prepare film by melt-pressing the polymer. However, only the products from the cyclohexene and the cyclohexane derivatives were sufficiently high in molecular weight to allow drawing and orientation studies. The others were too brittle to draw. Crystalline melting points were determined in the usual way on a Kofler hot stage between crossed polaroids. Data are collected in Table IV.

Residual unsaturation in polymers from unsaturated monomers was checked by infrared and bromine addition. It was assumed that no rearrangement of the carbon skeleton had occurred.

Preparation and polymerization of 7-oxaspiro[3.2]hexane. The monomeric compound (b.p. 103°/760 mm.) was prepared according to Searles and Lutz[11] from bis(chloromethyl)oxetane. This monomer, polymerized as above with phosphorus pentafluoride, gave a solid, crystallizable polymer with a crystalline m.p. of 45°. X-ray showed high crystallinity and high perfection.

Copolymer from bis(chloromethyl)oxetane and 2-oxa-7-methyl-Δ^6-spirononene. A mixture of 26.6 g. of freshly distilled 3,3-bis(chloromethyl)oxetane and 1.4 g. of freshly distilled 2-oxa-7-methyl-Δ^6-spirononene was polymerized in 250 ml. boiling methyl chloride in the usual manner with phosphorus pentafluoride. Vigorous boiling occurred when the catalyst was introduced in the reaction mixture, and the solution turned yellow. Polymer separated immediately. After evaporation of the solvent the polymer was washed with alcohol, which removed the yellow color; it was subsequently dried in a vacuum oven at 80°. The yield of the white finely divided polymer was 24 g. A clear, waxy film was pressed at 180° from the dry polymer. Strips of this film could be hand-drawn at room temperature *ca.* 6X. After boil-off in acetone, taut for 30 min., relaxed 5 min., the crystalline m.p. was 159–160°. X-ray diagram of such a strip showed the polymer to have high crystallinity and very high orientation.

Anal. Calcd. for $(C_5H_8OCl_2)_n$: C, 38.7; H, 5.2; Cl, 45.7. Calcd. for $(C_9H_{14}O)_n$: C, 77.4; H, 9.7; Cl, 0.0. Calcd. for 17:1 copolymer: C, 40.6; H, 5.4; Cl, 43.6. Found: C, 40.7, 40.9; H, 5.5, 5.6; Cl, 44.1, 44.3.

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(19) This compound is sold by the Ozark-Mahoning Co. under the tradename of "Phosfluogen A."

[CONTRIBUTION FROM THE MARSHALL LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Transannular Polymerization of 2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene

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2-Carbethoxybicyclo[2.2.1]-2,5-heptadiene (I) has been polymerized to a high molecular weight, soluble polymer believed to contain nortricyclene repeating units. Attempted polymerizations of structures similar to I suggest that this type of transannular polymerization of bicycloheptadienes requires activation of the double bonds and resonance stabilization of radicals formed during the polymerization.

The polymerizability of 2-substituted bicyclo-[2.2.1]-2,5-heptadienes has not been studied and little has been reported on the structure and properties of polymers of closely related bicycloheptadienes.[1-3] It has been found[4] that 2-carbethoxybicyclo[2.2.1]-2,5-heptadiene, I, polymerizes readily with free radical catalysts to give high molecular

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(1) A. A. Petrov and N. P. Sopov, *Zhur. Obshchei Khim,* **23**, 1034–1038 (1953).