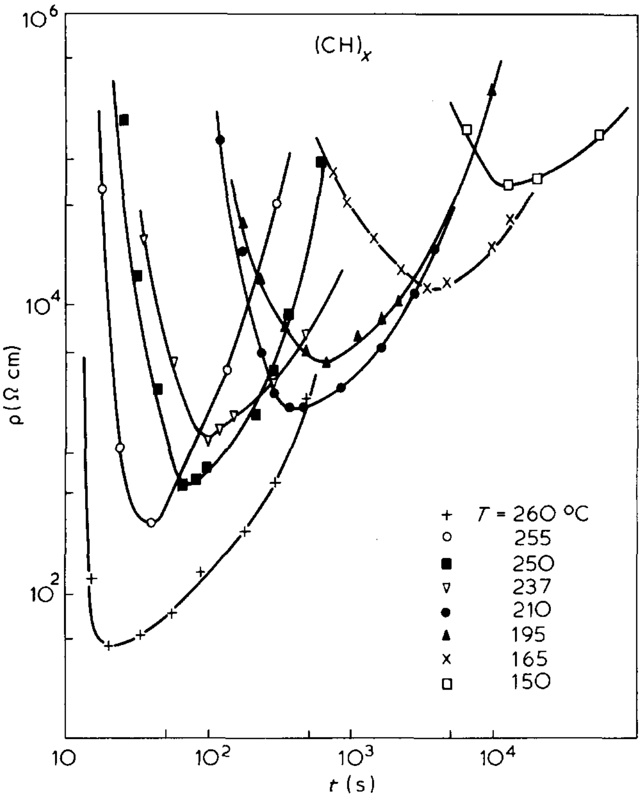

Figure 2 Time dependance of the resistivity of undoped (CH)$_x$ films during the isomerization process at different temperatures between 150° and 260°C. Starting point at t = 0 corresponds to almost entirely *cis*-(CH)$_x$ films with $\rho \sim 10^9$ Ωcm

Sample 1–isomerized at 200°C for 5 min (corresponding to t_{min} for this temperature), and doped with iodine vapour for 10 h.

Sample 2–isomerized at 200°C for 20 h and doped with iodine vapour for 10h.

From these results it is then clear that:

(i) the resistivity of an iodine doped *trans*-(CH)$_x$ isomerized during the time t_{min} is smaller than any published value[8];

Table 1

I_2 doped *cis*—(CH)$_x$	I_2 doped *trans*—(CH)$_x$*	Sample 1	Sample 2
~10^{-2} Ωcm	~2×10^{-2} Ωcm	~5×10^{-3} Ωcm	~1 Ωcm

* *Trans*—(CH)$_x$ used here was obtained in the usual way, i.e. by the isomerization of the *cis*-isomer at 200°C for 1 h

(ii) isomerization performed during times long compared with t_{min} induces so many defects that doping cannot be effective, leading to greater resistivities.

A systematic study of the effects of thermal treatment on undoped and doped (CH)$_x$ is in progress.

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Stereoselectivity of the ring-opening polymerization of bicyclo[6,1,0]nonene-4

A. I. Syatkowsky, T. T. Denisova, N. A. Buzina and B. D. Babitsky
S. V. Lebedev All-Union Research Institute of Synthetic Rubber, Leningrad, USSR

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Ring-opening polymerization of cycloolefins yields high molecular weight polyalkenamers containing double-bonds of both *cis*- and *trans*-configurations. Since the total amount of double bonds present in the system is not changed during the cycloolefin polymerization (the degree of unsaturation of polyalkenamers usually amounting to 100%), the polymer microstructure can be characterized by a single parameter, the proportion of *cis*- units in the polymer (the S value). The investigation of the stereoselectivity of cycloolefin polymerization is, however, often complicated by the fact that the double bonds formed undergo effective isomerization and the polymer microstructure is appreciably changed with conversion[1–3].

By extrapolating s to zero conversion an S_0 value can be obtained which is independent of the monomer concentration and the concentration of catalyst components and their ratio but varies with the polymerization temperature. This was previously demonstrated by our studies on cyclooctene (CO) polymerization[3].

Using the assumption that one active site can afford two types of structure, *cis* and *trans*, the S_0 value is the stereoselectivity of the elementary process of cycloolefin

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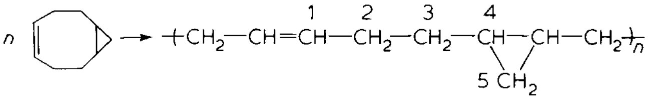
Table 1 Dependence of S_0 on the polymerization temperature in the ring-opening polymerization of BCN and CO

	$S_0 = \lim_{x \to 0} S(x)$	
t (°C)	BCN (±0.02)	CO (±0.01)
+2°	0.70	0.77
+15°	–	0.70
+18°	0.67	–
+28°	–	0.65
+41°	0.64	0.59
+63°	0.62	–

ring opening.

To study the effect of the cycloolefin structure on the stereoselectivity of the elementary process of cycloolefin ring opening we investigated the polymerization of bicyclo[6,1,0]nonene-4 (BCN) with WCl_6–$[(i\text{-}Bu)_2Al]_2O$ (TBAO) catalyst system in toluene at different temperatures. The polymerization conditions were chosen so as to minimize secondary isomerization of the polymer chain[3].

The BCN polymerization is described by the following scheme[4]:



The experimentally determined dependence of the proportion of *cis*-units in the polymer (S) on conversion (X) was extrapolated to $X=0$ and the values obtained (*Table* 1) were compared with those derived previously for cyclooctene polymerization[3].

The data in *Table* 1 show that the S_0 value decreases with increasing temperature in both cases, the $\log(S_0/1-S_0)$ *versus* $1/T$ relationship being linear over the temperature range studied (*Figure* 1).

It is seen from *Figure* 1 that with BCN the stereoselectivity of ring-opening is considerably less dependent on temperature than in the case of CO. Comparison of ^{13}C n.m.r. spectra of the monomers demonstrates that the electron distribution at the reaction site (the double bond) is essentially the same for both monomers (the chemical shifts for olefinic carbons in $CDCl_3$ are 131.2 and 130.8 ppm for CO and BCN, respectively). It is believed that the variation of S_0 with T depends on the ability of the cycloolefin methylene groups to provide the most favourable configuration of the transition state during the incorporation of cycloolefin into the polymer chain.

Experimental

Bicyclo[6,1,0]nonene-4 was prepared from cyclooctadiene-1,5 according to the procedure in reference 4 and contained >98% of the main reaction product, as demonstrated by the g.l.c. Tetraisobutylalumoxane (TBAO) was synthesized by the procedure in reference 5. The polymerization was carried out in toluene in a dry argon atmosphere and terminated by adding ethanol. The reaction was allowed to proceed for 2–5 h depending on the polymerization temperature. The ratio $[TBAO]/[WCl_6]=0.75 \div 1$; $[BCN]/[WCl_6]=200 \div 300$; $[BCN]=1.3\text{–}2.5$ mol l^{-1}. The intrinsic viscosity of the polymers was = 0.6–1.0 (in toluene). The polymer microstructure was studied by i.r. spectroscopy (1% solution in CCl_4). Bands at 3000 and 965 cm^{-1} were used for *cis*- and *trans*- structures, respectively. The microstructure of some samples was also studied by ^{13}C n.m.r. spectroscopy (10% solution in $CDCl_3$ with TMS as internal standard). The ^{13}C n.m.r. spectra of the polymers obtained show the following signals only (for signal numbers see the scheme given in the text): 130.36 ppm (*trans* 1), 129.85 ppm (*cis* 1), 33.25 ppm (*trans* 2), 29.15 ppm (3), 27.90 ppm (*cis* 2), 15.77 ppm (4), 11.14 ppm (5). The microstructure data obtained by the two methods were in good agreement. The i.r. spectra were recorded on a Specord-75 IR Carl Zeiss spectrophotometer (Jena). The ^{13}C n.m.r. spectra were obtained with a Bruker HX^{270} spectrometer operating at 67.88 MHz.

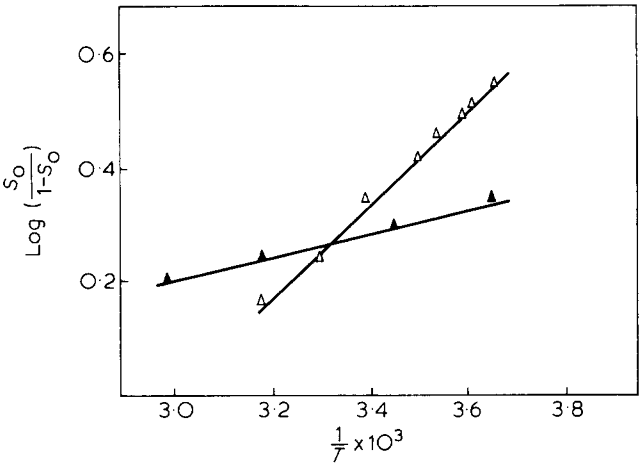


Figure 1 Plot of $\log(S_0/1-S_0)$ *versus* $1/T$ obtained using experimental data for BCN (▲) and CO (△)

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