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SYNTHESIS OF OPTICALLY ACTIVE POLYMERS OF PROPYLENE OXIDE ON ASYMMETRIC CATALYSTS

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Asymmetric synthesis of polymers attracted particular attention of scientists for last years in connection with modelling of biological processes. The most successes in this field were achieved in polymerization of olefine and diene monomers with using as catalysts of metal alkyls and alkoxides containing optically active radicals$^{1-3)}$.

However, there are only isolated successful attempts of preparation of optically active polymers from monomers of other types$^{4-5)}$. This article is concerned with asymmetric synthesis of propylene oxide polymers and partial separation of racemic propylene oxide into optical antipodes with the help of polymerization on neutral magnesium d(+)-tartrate. Magnesium d(+)-tartrate was obtained from basic magnesium carbonate and tartaric acid as in$^{6)}$. The dihydrate thus obtained was dehydrated in a dessicator over sulfuric acid for some days. Anhydrous magnesium d(+)-tartrate was prepared also by pouring hot aqueous solution of magnesium acetate into heated to 60° solution containing equivalent quantity of d(+)-tartaric acid and following boiling for 1 hour. White precipitate of tartrate formed was filtered, washed by water till neutral reaction and dessicated at 110°C.

Magnesium d(+)-tartrate thus obtained had $(\alpha)_D^{20} = +33.6$

±0.6° (C=0.580g in 100 ml of water, l=190.13 mm. According to[7]), $(\alpha)_D$=35.8°.

Polymerization of d,l-propylene oxide was carried out in bulk of monomer (without solvent). The sequence of operation was as follows: heating of catalyst at 70-75° in vacuum, freezing of monomer into calibrated glass ampula and sealing the ampula when submerged in liquid nitrogen during continuous pumping out of vacuum installation. After some time the ampula was weighed and unsealed, the catalyst was separated by centrifuging, the monomer which had not reacted was distilled into a tube, cooled down to -78°. Residuum of polymer was kept at pressure -0,01mm Hg during 1-2hours. The polymers thus obtained had high optical activity even without preliminary fractionation. The results of experiments are presented in table 1.

Table 1.

Polymerization of d,l-propylene oxide on d-magnesium tartrate.

N° of experiments	Weight of catalyst g	Weight of initial monomer	Polymer					
			Yield %	α_D	Concentration in benzene g/100 ml	$(\alpha)_D$	$(M)_D^{xx}$	$(\eta)^{xxx}$ 100 ml/g
I-B-25	0.223	4.352	10.3	-0.190	2.07	-9.2±0.7	-5.30	0.03
2-B-49	0.153	4.472	4.32	-0.084^x	1.12	-15.6±0.6	-9.05	0.24
3-B-70	0.590	8.368	1.67	-0.847	3.09	-27.4±0.4	-15.9	0.11

x) in tube 480 mm long; xx) per one monomer unit;
xxx) in benzene solution at 25°C.

Optical activity of polymer solution in benzene as well as that of propylene oxide was measured by means of polarimeter "Hilger and Watts" in tubes of 100 mm long; accuracy of reading was ±0.005-0.007°. The figures with signs ± in seventh column of table mean average quadratic error of reading. From a rough estimation of molecular weight $\bar{M}_W$ of polymers by the use of formula $(\eta)=1{,}12\times10^{-4}\ \bar{M}_W^{0.77}$ (see[8]) it was calculated that polymers 2-B-49 and 3-B-49 and with $\bar{M}_W=20000$ and 7700 correspondingly could contain as a maximum one fragment of tartaric acid per 70-180 monomer units. Molecular rotatory power of d-tartaric acid $(M)_D$ is 21.08° [7] and maximal contribution of it to optical activity of polymer can be equal to $+0.12$-0.30°. Observed optical activity of polymers considerably exceeds this value and differs from it by sign. It is apparent that it can not be explained by the presence of optically active end groups. In order to confirm the existence of asymmetric synthesis optical activity unchanged monomer was measured in experiment giving the highest yield of polymer (I-B-25). The monomer which had not reacted had $(\alpha)_D^{18} = -0.282 \pm 0.007^{\circ}$. It is known[9] that l(+)-propylene oxide forms a polymer which rotates to the left in benzene solution. Therefore, the signs of optical activity of obtained polymers and unchanged propylene oxide point out that on the surface of magnesium d-tartrate only l(+)-propyleneoxide polymerizes whereas unreacted monomer enriches itself with optical isomer of opposite configuration.

Therefore, the catalyst used reproduces in principle stereospecific action of ferments and can serve for partial resolution of racemic propylene oxide into optical antipodes by means of stereospecific polymerization.

Catalytic activity of magnesium d-tartrate was considerably lower than the activity of homogeneous system diethylzinc -l-borneol-toluene used by Japanese authors[10]. The polymerization proceeded in experiment 3-B-70 (see table 1) for 45 hours at 130-150° and in experiments 1-B-25 and 2-B-49 for 13,5-17 months at room temperature. However, asymmetric effects observed by us exceed by 3-7 times the effect obtained in[10]. The essential feature of the system investigated in this work is its heterogeneity. An interesting peculiarity of propylene oxide polymerization on magnesium d-tartrate is the decrease of optical activity of polymers with degree of conversion, as can be seen from table 1; polymer which was obtained in the first stages of polymerization is apparently optically pure, as maximum specific rotatory power of crystalline polypropylene oxide was -28.6° according to Nan Shi-Chu and Price[11]. Such a deterioration of asymmetric action of catalytic system was also observed by Farina and Bressan[12] in asymmetric synthesis of polybenzofuran.

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