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Abstract

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POLYMERIZATION OF ALLYLCYCLOPENTANE IN THE PRESENCE OF THE CATALYTIC SYSTEM $TiCl_4 + Al(iso\text{-}C_4H_9)_3$

The polymerization of naphthenic hydrocarbons with an unsaturated side chain began to be studied only in recent years. Polymers with a branched side chain possess a higher melting point, greater elasticity, higher solubility, and greater adhesion than linear polymers. The synthesis of polyallylcyclopentane has been described in the literature only by Campbell and Havin (^{1}). The solid polymer obtained in the polymerization of allylcyclopentane in the presence of titanium tetrachloride and tetraethylaluminum had a melting point of 225° and at 250° readily formed fibers and transparent films. Allylcyclopentane was synthesized by us according to the following reaction scheme:

$$\text{cyclopentanone} \xrightarrow{+H_2} \text{cyclopentanol} \xrightarrow{HCl} \text{chlorocyclopentane} \xrightarrow{Mg} \text{cyclopentylmagnesium chloride} \xrightarrow{CH_2}$$

allylcyclopentane

Cyclopentanone was obtained by heating adipic acid in the presence of barium hydroxide. Hydrogenation of cyclopentanone was carried out in an autoclave in the presence of Raney nickel at room temperature (yield 84% of theoretical). Chlorocyclopentane was obtained by treating cyclopentanol with three volumes of concentrated hydrochloric acid at the boiling temperature of the mixture for three hours, with a yield of 67% of theoretical. All physicochemical constants of the intermediate compounds synthesized by us correspond to those described in the literature. The synthesis of allylcyclopentane was carried out by the Grignard reaction from allyl bromide and cyclopentylmagnesium chloride.

To find the optimal conditions for this synthesis, we tried various methods and settled on the method of Resseguier (^{2}), which is practically easy to carry out and gives comparatively high yields of product (up to 57% of theoretical). The target fraction of allylcyclopentane was purified by boiling and distillation over metallic sodium on a column. A fraction was collected with b.p. 125.7-126.3/757 mm, having d_4^{20} 0.7941, n_D^{20} 1.4400; MR_D found 36.59, calculated 36.47; elemental composition

Found, %: C 86.97; H 13.02
Calculated, %: C 87.20; H 12.80

Literature data for allylcyclopentane ([3]): b.p. 124-124.5/756; d_4^{20} 0.7912; n_D^{20} 1.4400; ([4]): b.p. 125.8-126.5/737; d_4^{20} 0.7939, n_D^{20} 1.4408.

For the synthesized allylcyclopentane, an infrared spectrum was taken, which proved to be completely identical with the reference spectrum* and showed no presence of any impurities.

Polymerization was carried out both in an open system and in ampoules, at 70° in a stream of nitrogen, using the catalyst $TiCl_4 + Al(iso\text{-}C_4H_9)_3$ and *n*-heptane as solvent according to the generally accepted method. Titanium tetrachloride was used in the form of a 1 M solution in *n*-heptane; the concentration of triisobutylaluminum was 0.395 g/ml.

* The authors express their deep gratitude to M. M. Kusakov, M. V. Shishkina, and E. A. Prokof' eva for their study of the infrared spectra of our substances.

Table 1

Dependence of polyallylcyclopentane yields on the conditions of polymerization

Experiment No.	Monomer, mmol	$Al(iso\text{-}C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti molar	Polymerization temp., °C	Polymerization duration, h	Yield of solid polymer, % of monomer charged	Softening temp., °C	Note
										Polymerization in ampoules
1	60	3	3		1 : 1	70	5	40,3	214—220	Catalyst was aged *
4	60	3	3	68 (10 ml)	1 : 1	70	5	60,8	200—202	Catalyst was not aged
9	60	3	3	68	1 : 1	70	5	51,7	206—210	Catalyst was aged
25	60	6	6	68	1 : 1	70	5	38,0	202—212	Poor stirring

Experiment No.	Monomer, mmol	Al(iso-$C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti molar	Polymerization temp., °C	Polymerization duration, h	Yield of solid polymer, % of monomer charged	Softening temp., °C	Note
22	60	4	2	68	2 : 1	70	5	34,8	206—208	Poor stirring
3	60	4	2	68	2 : 1	70	5	71,0	205—220	Ordinary stirring
18	60	4	2	68	2 : 1	70	10	37,8	205—209	Monomer stored for a long time at room temperature
19	30	4	2	103 (15 ml)	2 : 1	70	10	36,4	210—215	Monomer stored for a long time
12	30	4	2	103	2 : 1	70	5	61,0	207—209	

Experiment No.	Monomer, mmol	Al(iso-$C_4H_9)_3$, mmol	$TiCl_4$, mmol	n-Heptane, mmol	Al : Ti molar	Polymerization temp., °C	Polymerization duration, h	Yield of solid polymer, % of monomer charged	Softening temp., °C	Note
13	60	4	2	68	2 : 1	70	10	26,5	202—205	Cooling of the ampoule with dry ice during filling
14	60	4	2	68	2 : 1	70	15	27,2		
24	30	3	3	103	1 : 1	70	5	60,5	200—210	
23	30	4,5	1,5	103	3 : 1	70	5	39,4	200—206	
47	30	4,8	1,2	103	4 : 1	70	5	7,6	210—217	
2	60	6	2	68	3 : 1	70	5	27,3	191—196	
11	30	2	1	103	2 : 1	70	5	45,5	214—222	
21	60	8	4	68	2 : 1	70	5	53,2	216—218	Catalyst was not aged
56	30	4	2	103	2 : 1	70	42	66,5	220—231	
27	60	3	3	0	1 : 1	70	5	32,0	190—208	Polymerization in bulk
6	60	4	2	0	2 : 1	70	5	33,4	215—225	Same

Experiment No.	Monomer, mmol	Al(iso-$C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti molar	Polymerization temp., °C	Polymerization duration, h	Yield of solid polymer, % of monomer charged	Softening temp., °C	Note
										Polymerization in an open system
7	60	8	4	204	2 : 1	70	5	19,8	200—218	Catalyst was aged at 70° for 30 min
17	60	8	4	204	2 : 1	70	5	24,4	204—207	Catalyst was not aged
8	120	8	4	116	2 : 1	21	15	12,1	190—195	Room temperature
1a	30	5	5	336	1 : 1	70	5	31,2	210—222	
2a	30	5	5	336	1 : 1	70	5	38,2	210—222	
34	70	20	20	340	1 : 1	70	5	27,2	210—215	Catalyst was not aged

Experiment No.	Monomer, mmol	Al(iso-$C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti molar	Polymerization temp., °C	Polymerization duration, h	Yield of solid polymer, % of monomer charged	Softening temp., °C	Note
85	30	4	2	68	2 : 1	70	5	48,5		Catalyst was formed outside the system

* After the two catalyst components had been mixed, the ampoule was cooled to room temperature.

Decomposition of the catalyst was carried out with methanol acidified with hydrochloric acid, and the polymer was thoroughly washed with methanol and dried in vacuum at 80°. The most characteristic experiments on the polymerization of allylcyclopentane are given in Table 1. It was shown that adding the monomer immediately after mixing the catalyst components, or after cooling the ampoule, which heats up upon mixing the catalyst components, has little effect on the polymer yield (expts. 4 and 9). Aging the catalyst at 80° for 30 min somewhat reduced the polymer yield (expts. 7 and 17). If the catalyst components are mixed while cooling the ampoule with dry ice and the monomer is then added rapidly, the polymer yield also decreases, probably owing to a decrease in the rate of formation of active centers (expts. 3 and 13). Polymer yields fall when the temperature is lowered from 70° to room temperature (expts. 8 and 17), as well as with poor stirring (expts. 4 and 25; 3 and 22) and upon prolonged storage of the monomer (expts. 3 and 18; 12 and 19). Therefore it is desirable to introduce freshly redistilled monomer into the reaction (the infrared spectra of freshly prepared monomer and of monomer redistilled after prolonged storage are completely identical).

In polymerization in an open system the yields are considerably lower than in polymerization in ampoules (expts. 3 and 8; 12 and 17). However, the yields increase if the catalyst is formed outside the system in a small volume of solvent (expt. 85).

We studied the effect of the molar ratios of the catalyst components. At an Al : Ti ratio of 0.5 : 1, a rubber-like substance was obtained, completely soluble in ether. The optimum ratios are 1 : 1 and 2 : 1, at which the yields of solid polymer reach 71% (expts. 3, 4, 12, 24). With further increase in the Al : Ti ratio the polymer yield falls sharply (expts. 23 and 47). With increasing catalyst concentration in the reaction mixture, the polymer yield increases (expts. 11 and 12), but only up to a certain limit (expts. 3 and 21; 1a, 2a and 34; 17 and 37).

It was shown that the optimum polymerization time is 5 h; increasing it even to 42 h only slightly raises the polymer yield (expts. 1 and 4; 12 and 56). Carrying out the polymerization in bulk decreases the polymer yield (expts. 3 and 6; 4 and 27). When cyclohexane was used as the solvent, a viscous, oily polymer was obtained. Cationic polymerization of allylcyclopentane in the presence of $TiCl_4$ for 43 h at 70° did not give a solid polymer. The solid polyallylcyclopentane obtained was a white powder with a softening temperature within 200–220° for almost all samples. At elevated temperature the polymer was partially soluble in *n*-heptane and completely soluble in cyclohexane and benzene. The X-ray diffraction pattern of the unfractionated polymer* showed that the polymer is amorphous.

For combined polymer samples, successive extraction with boiling diethyl ether and *n*-heptane was carried out (see Table 2). The molecular weight of the fraction soluble in ether, determined by the cryoscopic method, was approximately 850. The elemental composition of the fractionated polymer showed the absence of traces of catalyst in the polymer.

Found, %: C 86.91; H 13.08
Calculated, %: C 87.20; H 12.80

The elemental composition was also determined for the fraction insoluble in ether. Found, %: C 87.04; H 12.96.

The melting temperature was determined with the aid of a polarizing microscope,** and it turned out that upon prolonged annealing well-formed crystals are obtained from the polymer. It was also shown that, upon prolonged boiling of the polymer in *n*-heptane, partial crystallization occurs, which is confirmed by X-ray structural analysis data, and its softening temperature increases (the polymer before 350° melts only partially). However, upon reprecipitation of this sample from cyclohexane it becomes amorphous and its softening temperature decreases to 215–220°. The difficulty of crystallization is evidently due to the special structure of the elementary units in the polymer, which form chains with clearly expressed steric hindrance.

Table 2

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* For taking the X-ray diffraction patterns we express our gratitude to V. V. Shchekin and F. V. Koreneskii.

** For determination of the melting temperatures we express our gratitude to G. V. Vinogradov and O. S. Khvatova.

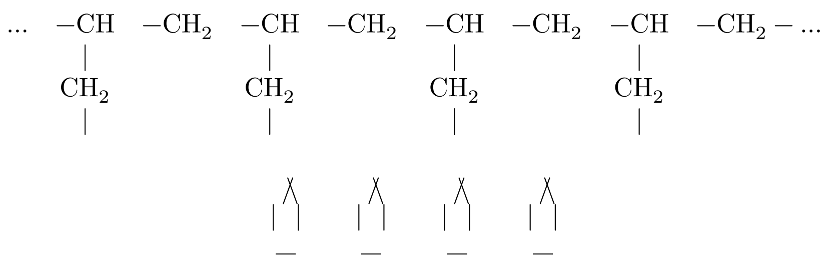
Fractionation of polyallylcyclopentane by the extraction method

Polyallylcyclopentane	Weight of the unfractionated polymer, g	Ether-soluble fraction: yield, %	Ether-soluble fraction: softening temp., °C	Ether-soluble fraction: intrinsic viscosity, $[\eta]^*$	*n*-Heptane-soluble fraction: yield, %	*n*-Heptane-soluble fraction: softening temp., °C	*n*-Heptane-soluble fraction: m.p., °C	*n*-Heptane-soluble fraction: intrinsic viscosity, $[\eta]^*$	*n*-Heptane-insoluble fraction: yield, %	*n*-Heptane-insoluble fraction: softening temp., °C	*n*-Heptane-insoluble fraction: m.p., °C	*n*-Heptane-insoluble fraction: intrinsic viscosity, $[\eta]^*$
Combined samples from experiments with the ratio Al : Ti = 1 : 1	9.05	25.2	67–80	0.15	36.2	238–250		1.11	38.6	210–222		1.3
Same, with the ratio Al : Ti = 2 : 1	24.18	26.5	100–120	0.16	42.3	—	232	1.17	31.2	226–232	243	1.2

Polyallylcyclopentane	Weight of the unfractionated polymer, g	Ether-soluble fraction: yield, %	Ether-soluble fraction: softening temp., °C	Ether-soluble fraction: intrinsic viscosity, $[\eta]^*$	n-Heptane-soluble fraction: yield, %	n-Heptane-soluble fraction: softening temp., °C	n-Heptane-soluble fraction: m.p., °C	n-Heptane-soluble fraction: intrinsic viscosity, $[\eta]^*$	n-Heptane-insoluble fraction: yield, %	n-Heptane-insoluble fraction: softening temp., °C	n-Heptane-insoluble fraction: m.p., °C	n-Heptane-insoluble fraction: intrinsic viscosity, $[\eta]^*$
Same, with the ratio Al : Ti = 3 : 1 and 4 : 1	4.84	54.0	100–125 ($M_n \simeq$ 1000)	0.15	22.6	210–223			23.4	220–230		1.2

* Determined in benzene at 30°.

It should be noted that the polymer fraction insoluble in n-heptane, after reprecipitation from cyclohexane, becomes very fibrous, as a result of which it was impossible to determine its melting temperature either by the polarization-microscope method or by recording a thermomechanical curve, and also impossible to record an infrared spectrum because of its tendency to oxidation. Recording of the infrared spectrum for the fractions soluble in ether and in n-heptane proved the structure of the polymer to be of the "head-to-tail" type:



For the fraction of polyallylcyclopentane insoluble in *n*-heptane, the weight-average molecular weight was determined in cyclohexane solution at 20° by the light-scattering method at a wavelength of 5461 Å**, and was found to be 170,000.

The liquid polymers obtained from the methanol extracts by precipitation with water were viscous yellowish oils boiling over a broad temperature interval.

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REFERENCES

1. T. W. Campbell, H. C. Haven, *J. Appl. Polym. Sci.*, **1**, 73 (1959).
2. M. B. Ressequier, *Bull. Soc. chim. France*, 7, 431 (1910).
3. R. Ya. Levin and N. N. Mezentseva, *Uch. zap. Moskovsk. univ.*, vol. 132, book 7, 241 (1950).
4. A. F. Platé, E. M. Mil' vitskaya, *Uch. zap. Moskovsk. univ.*, vol. 132, 248 (1950).

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Note: Figure translations are in progress. See original paper for figures.