Academician A. V. TOPCHIEV, E. L. FANTALOVA, L. V. OSIPOVA

Table 1

1962

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. V. TOPCHIEV, E. L. FANTALOVA, L. V. OSIPOVA

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

The field of polymerization of naphthenic hydrocarbons with an unsaturated side chain has begun to be developed only in recent years. The synthesis of polyallylcyclohexane, which has a high melting point and is capable of forming films and fibers, in addition to theoretical significance, is also of some practical interest. In the literature there is only one paper in which the preparation of polyallylcyclohexane in the presence of titanium tetrachloride and triethylaluminum is described and a brief characterization of the properties of this polymer is given ([1]).

Table 1

Polymerization of allylcyclohexane in the presence of the catalytic system $Al(iso\text{-}C_4H_9)_3$ + $TiCl_4$

No. of experiments	Monomer, mmol	$Al(iso\text{-}C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti, molar	Polymerization temp., °C	Reaction duration, h	Yield of solid polymer, wt. % per monomer	Softening temp., °C
Polymerization in ampoules									
42	60	3	3	68	1 : 1	70	5	7.5	210—225
49	60	6	6	68	1 : 1	70	5	12.4	125—220
40	60	4	2	68	2 : 1	70	5	traces	
45	30	4	2	103	2 : 1	70	5	16.6	208—218

No. of experiments	Monomer, mmol	Al(iso-$C_4H_9)_3$, mmol	$TiCl_4$, mmol	n-Heptane, mmol	Al : Ti, molar	Polymerization temp., °C	Reaction duration, h	Yield of solid polymer, wt. % per monomer	Softening temp., °C
46	60	4.8	1.2	68	4 : 1	70	5	4.0	220–224 (not all up to 270°)
55a	30	4	2	103	2 : 1	70	42	48.5	205–214
75	30	4	2	103	2 : 1	70	42	48.5	212–224
54a	30	3	3	103	1 : 1	70	42	61.0	208–218
72	30	3	3	103	1 : 1	70	25	69.5	232–262
74	30	3	3	103	1 : 1	70	20	73.5	225–239
63	10	0.8	0.8	110	1 : 1	70	42	0	Viscous oil
62a	10	1.6	1.6	110	1 : 1	70	42	37.0	202–225
626	10	1.6	1.6	110	1 : 1	70	42	37.0	202–230
Polymerization in an open system									
10a 11a	30	2	1	336	2 : 1	70	5	0	
5a	30	2.5	2.5	336	1 : 1	70	5	22.6	213–237
4a	30	2.5	2.5	336	1 : 1	70	5	28.2	216–233
7a	30	2.5	2.5	336	1 : 1	70	42	25.4	up to 231

No. of experiments	Monomer, mmol	$Al(iso-C_4H_9)_3$, mmol	$TiCl_4$, mmol	*n*-Heptane, mmol	Al : Ti, molar	Polymerization temp., °C	Reaction duration, h	Yield of solid polymer, wt. % per monomer	Softening temp., °C
9a	30	5	5	336	1 : 1	70	5	56.6	up to 237°
3a	60	10	10	672	1 : 1	70	5	55.9	212—238
2a	60	4	2	134	2 : 1	70	42	17.5	210—234

Allylcyclohexane was synthesized by us from cyclohexylmagnesium chloride and allyl bromide according to the slightly modified procedure of R. Ya. Levina (2). The allylcyclohexane obtained in 55.6% yield, after boiling and distillation over metallic sodium, had the following physicochemical constants: b.p. 152—153°/757 mm Hg, d_4^{20} 0.8206, n_D^{20} 1.4510; MR_D found 40.77, calculated 41.09; elemental composition:

Found, %: C 86.99; H 13.01
Calculated, %: C 87.02; H 12.98

(The allylcyclohexane synthesized by R. Ya. Levina and F. F. Tsurikov had the following constants: b.p. 151—152°, d_4^{20} 0.8155; n_D^{20} 1.4510.)

Recording the infrared spectrum of the monomer showed the absence of impurities.* Polymerization of allylcyclohexane was carried out both in an open system and in ampoules according to generally accepted procedures at 70°, in a nitrogen atmosphere, in *n*-heptane. The most characteristic experiments are given in Table 1.

In the polymerization of allylcyclohexane in ampoules under conditions optimal for the polymerization of allylcyclopentane ** (experiments 42, 40, 45), insignificant yields of solid polymer are obtained even at high catalyst concentration (experiment 49). Increasing the molar ratio of the catalyst components $Al(iso-C_4H_9)_3 : TiCl_4$ to 3 : 1 and 4 : 1 likewise does not increase the yield of solid polyallylcyclohexane (experiment 46).

Only with an increase in the polymerization time to 20 or more hours were high polymer yields achieved. In long experiments, the influence of the catalyst concentration begins to be sharply manifested (experiments 62 and 63).

In the polymerization of allylcyclohexane at atmospheric pressure, as in polymerization in ampoules, the optimal molar ratio of the catalyst components proved to be 1 : 1.

The decisive factor in this case is the catalyst concentration (experiments 10a, 4a, 9a). In contrast to ampoule polymerization, the optimal time for polymerization in an open system proved to be 5 h.

It should be noted that parallel experiments show good agreement of the results (experiments 62a, 62b, 3a, 4a, 5a).

Table 2

Fractionation of polyallylcyclohexane by the extraction method

Polymer	Ether-soluble fraction: fraction content in polymer, %	Ether-soluble fraction: softening temperature, °C	Ether-soluble fraction: characteristic viscosity, η**	n-heptane-soluble fraction: fraction content in polymer, %	n-heptane-soluble fraction: softening temperature, °C	n-heptane-soluble fraction: characteristic viscosity, η
Obtained by polymerization in an open system	20—40	95—115m.p. —237*	0.26M = 600—800(cryoscopy)0.26	60—80	210—224m.p. 263°	0.29 reprecipitated.$M = 6 \cdot 10^4$ 0.5—unreprecipitated
Obtained by polymerization in ampoules	29—37	up to 120°m.p. —243		71—63		0.37

* The melting temperature was determined by the polarization-microscope method.
** Determined in benzene at 30°C.

The solid polymer obtained, a white, finely dispersed powder, was fractionated in a Soxhlet apparatus by successive treatment with boiling diethyl ether and n-heptane (see Table 2). In contrast to polyallylcyclopentane, all polyallylcyclohexane is soluble in boiling n-heptane.

As X-ray structural analysis showed ***, both fractions are amorphous.

Fig. 1. Thermomechanical curve for the fraction of polyallylcyclohexane soluble in n-heptane

Figure 1: Fig. 1. Thermomechanical curve for the fraction of polyallylcyclohexane soluble in n-heptane

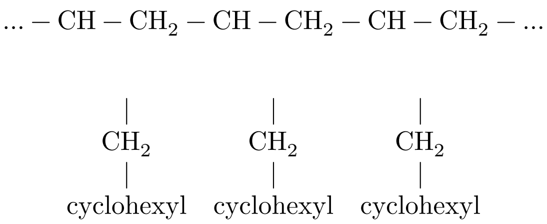
However, when the melting point was determined by the polarization-microscope method, after prolonged annealing of the polymer, well-formed crystals were obtained.*

Found, %: C 86.96; H 12.94
Calculated, %: C 87.02; H 12.98

The elemental composition indicates the absence of catalyst impurities in the polymer.

The weight-average molecular weight, determined for the fraction of polyallylcyclohexane soluble in *n*-heptane by the light-scattering method at $\lambda = 5461$ Å, proved to be 60000.**

The infrared spectrum of polyallylcyclohexane showed the presence in the polymer of a monosubstituted cyclohexane ring, CH_2 groups, and a small amount of methyl groups, which are apparently terminal. In addition, the polymer contains no polymethylene chains with more than five methyl groups. Comparison with the spectrum of 2,4-dimethylhexane showed that addition of the individual polymer units occurs in a "head-to-tail" manner and, consequently, the polymer has the structure:



$$\begin{array}{ccccccccccccc} \ldots & - & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{CH} & - & \mathrm{CH_2} & - & \mathrm{CH} & - & \mathrm{CH_2} - \ldots \\ & & | & & & & | & & & & | & & \\ & & \mathrm{CH_2} & & & & \mathrm{CH_2} & & & & \mathrm{CH_2} & & \\ & & | & & & & | & & & & | & & \\ & & \text{cyclohexyl} & & & & \text{cyclohexyl} & & & & \text{cyclohexyl} & & \end{array}$$

Fig. 1. Thermomechanical curve for the fraction of polyallylcyclohexane soluble in *n*-heptane.

Figure 1 gives the thermomechanical curve for the polymer fraction soluble in *n*-heptane.***

---

* The authors express their gratitude to M. M. Kusakov, M. V. Shishkina, and E. A. Prokof' eva for recording the infrared spectra.
** The article devoted to the polymerization of allylcyclopentane is in press.
*** The authors express their gratitude to V. V. Shchekin and F. V. Korenevskaya for taking the X-ray patterns.

Liquid polymers, precipitated with water from methanolic solutions, are viscous liquids boiling over a wide temperature range.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
24 VIII 1962

REFERENCES

1. T. W. Campbell, A. C. Haven, *J. Appl. Polym. Sci.*, **1**, 73 (1959).
2. R. Ya. Levina, F. F. Tsurikov, *ZhOKh*, **4**, 1250 (1934).

* For the determination of the melting temperatures we express our gratitude to G. V. Vinogradov and O. S. Khvatova.
** For the determination of the molecular weight the authors express their gratitude to M. M. Kusakov, Yu. A. Koshevnik, and E. A. Razumovskaya.
*** For recording the thermomechanical curve the authors express their gratitude to G. L. Slonimsky.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.