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Abstract

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POLYMERIZATION OF CERTAIN COMPOUNDS WITH TWO ISOPROPENYL GROUPS

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In studying the process of dimerization of α-methylstyrene under the influence of ionic-type catalysts—$SnCl_4$, $TiCl_4$, $AlCl_3$—it was shown that at elevated temperature (70–100°) there occurs the formation exclusively of a dimer, a saturated crystalline product (^{1},^{2}). By direct synthesis (^{2}) it was convincingly demonstrated that the saturated dimer is 1,1,3-trimethyl-3-phenylindane.

$$2\,CH_2{=}C(CH_3)Ph \longrightarrow \text{1,1,3-trimethyl-3-phenylindane}$$

I

Similar dimerization products are also formed by certain other α-methylstyrenes substituted in the ring. Thus, under definite conditions, α-methylstyrene behaves as a monofunctional compound.

It seemed of interest to investigate the behavior of compounds containing two isopropenyl groups under conditions analogous to those for the formation of the saturated dimer of α-methylstyrene. In other words, a series of bifunctional compounds was studied with the aim of obtaining linear polymers containing benzene rings in the main chain. It could be expected that, under certain conditions, a bifunctional compound, such as, for example, 1,4-diisopropenylbenzene, would react in the following way:

$$2\,CH_2{=}C(CH_3){-}C_6H_4{-}C(CH_3){=}CH_2 \longrightarrow \text{dimeric product with an indane ring and a remaining isopropenyl}$$

$$n\,CH_2{=}C(CH_3){-}C_6H_4{-}C(CH_3){=}CH_2 \longrightarrow$$

$$\longrightarrow \quad \text{[structural formula of polymer fragment II, with } (n-2) \text{ repeat units]} \qquad \text{(II)}$$

We synthesized and characterized the following bifunctional compounds:

1,4-diisopropenylbenzene (3) (m.p. 64–64.5°)
III

4,4'-diisopropenyldiphenylmethane (m.p. 54.5–55°)
IV

4,4'-diisopropenyldiphenylethane (m.p. 124–124.5°)
V

The compounds obtained were subjected to polymerization in toluene solution in the presence of $SnCl_4$ and the cocatalyst HCl. In all cases, polymers were obtained that are soluble in benzene and its homologues, in carbon tetrachloride, carbon disulfide, and some others, and insoluble in alcohols. After

Table 1

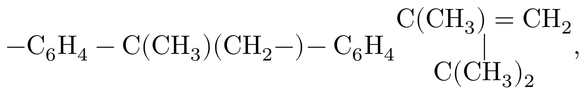
Monomer	$[\eta]$	M	Solubility
III	0.07	$7.0 \cdot 10^3$	in C_6H_6, CCl_4, CS_2, hexane
IV	0.30	–	in C_6H_6, CCl_4, CS_2
V	0.70	$7.8 \cdot 10^5$	in C_6H_6, CCl_4, CS_2

[structural formula of polymer VI with repeat unit n] (VI)

$$[-R - C_6H_4 - C(CH_3)(CH_2-)- C_6H_4 - C(CH_3)_2 - R-]_n$$

VII

$$R = -CH_2-,\ -C_2H_4-$$



$$-C_6H_4 - C(CH_3)(CH_2-)- C_6H_4 \begin{matrix} C(CH_3) = CH_2 \\ | \\ C(CH_3)_2 \end{matrix},$$

After reprecipitation the polymers are obtained in the form of white powders. Some properties of the polymers obtained are given in Table 1.

The elemental composition of all the polymers obtained agrees exactly with the elemental composition of the corresponding starting monomers. The polymers are saturated and do not add bromine. The structure of the polymer of 1,4-diisopropenylbenzene may be represented by formula VI, and the structure of the polymers of 4,4′-diisopropenyldiphenylmethane and 4,4′-diisopropenyldiphenylethane by formula VII.

In view of the exceptional resistance of the polymers to oxidative and thermal degradation, it was not possible to obtain any individual products of oxidation or decomposition. However, the similarity of the infrared spectra of the polymers and of 1,3,6-trimethylindan (4), chosen as a model compound, apparently speaks in favor of structures VI and VII. Investigations of the optical properties of polymer solutions, carried out in the laboratory of Prof. V. N. Tsvetkov by S. Ya. Magarik, to whom the authors express their great gratitude, convincingly show that the benzene rings are located in the main chain of the polymer (5).

Thus, it has been shown that, under certain conditions, linear polymers can be obtained on the basis of compounds of the type

$$CH_2{=}C(CH_3) - C_6H_4 - R - C_6H_4 - C(CH_3){=}CH_2$$

where R is any atom or group of atoms that does not react (in the broad sense of the word) with ionic-type catalysts.

Fig. 1. Absorption spectra in the infrared region (4.5% on an ISP-14-B instrument, NaCl prism):
a –poly-1,4-diisopropenylbenzene;
b –poly-4,4′-diisopropenyldiphenylmethane;
v –poly-4,4′-diisopropenyldiphenylethane;
g –1,3,6-trimethylindan.

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