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Abstract

Full Text

Chemistry

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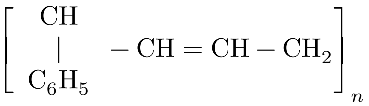
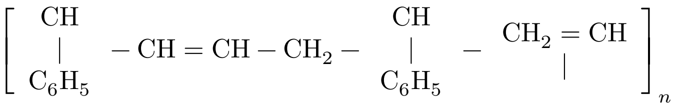
Stereospecific Polymerization of trans-1-Phenylbutadiene-1,3

(Presented by Academician V. A. Kargin, 20 VI 1963)

In the stereospecific polymerization of substituted butadienes, depending on the polymerization conditions, stereoregular polymers with different intramolecular structures can be obtained from one and the same monomer. The structure of the polymers formed is related not only to the polymerization conditions, but also to the nature and chemical structure of the diene monomers. Thus, in the case of 1-phenylbutadiene-1,3, the introduction of a phenyl group of considerable volume will exert a strongly pronounced influence on the structure of the polymer obtained. If one considers atomic models of polymers of 1-phenylbutadiene-1,3, then, proceeding from the considerable steric hindrance caused by the presence of phenyl groups, one can predict that the trans-1,4-structure (I) is more probable than the cis-1,4-structure. The possibility of 1,2- and 3,4-structures is not excluded. The first of these structures is associated with large steric hindrances, which lead to alternation of this structure with the 1,4-structure.



$$\left[\begin{matrix}\mathrm{CH}\\ |\\ \mathrm{C_6H_5}\end{matrix} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2}\right]_n \qquad \text{(I)}$$



$$\left[\begin{matrix}\mathrm{CH}\\ |\\ \mathrm{C_6H_5}\end{matrix} - \mathrm{CH} = \mathrm{CH} - \mathrm{CH_2} - \begin{matrix}\mathrm{CH}\\ |\\ \mathrm{C_6H_5}\end{matrix} - \begin{matrix}\mathrm{CH_2} = \mathrm{CH}\\ \qquad\quad |\end{matrix}\right]_n \qquad \text{(II)}$$

Until the present time, the homopolymerization of 1-phenylbutadiene has been little studied. From the literature it is known that, in the polymerization of 1-phenylbutadiene-1,3, dimers are predominantly formed (^{1}). In 1953 a paper appeared (^{2}) on the polymerization of this monomer by various methods: emulsion polymerization, in the presence of Na, $SnCl_4$, and γ-radiation. Study of the structure of the polymers, both by a chemical method and with the aid of infrared spectroscopy, showed that the polymers obtained contain up to 60% of 1,4-, some amount of 1,2-, and an insignificant amount of 3,4-structure. The properties of the polymers have been little investigated (softening temperature 60–70°, soluble in many organic solvents).

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Fig. 1

Figure 1: Fig. 1

Investigation of the reaction of stereospecific polymerization of phenyl-substituted butadienes is of interest from the point of view of broadening our ideas about the mechanism of formation of stereoregular polymers of different structure from monomers with conjugated bonds.

In this connection we investigated the polymerization of trans-1-phenylbutadiene-1,3 with the aid of the complex catalyst $TiCl_4$ + Al(iso-$C_4H_9)_3$ at 25° in hydrocarbon solvents. The polymers obtained, which were white solid powders, were extracted successively with acetone (up to 50%), diethyl ether (up to 25%), and the remaining amount dissolved completely in benzene or toluene. All samples have a relatively low logarithmic reduced viscosity, equal to 0.11 (0.25% solution in toluene at 30°). The melting temperature varies within the range 105-120°. The yield of polymers depends both on the nature of the solvent (in benzene, 80%; in heptane, 30%) and on the polymerization time, while the structure of the polymers changes hardly at all (according to infrared-spectral data).

In order to carry out a qualitative study of the chemical structure of the polymers, spectra were obtained on an IKS-14 spectrophotometer using NaCl and LiF prisms. The samples were examined as films prepared from benzene solution. The following features are observed in the IR spectra (Fig. 1).

1) The bands at 694 and 745 cm^{-1} characterize the phenyl group. The equal intensities of these bands indicate that the phenyl group is attached to a tertiary carbon atom. Conjugation of the C=C bond with the phenyl group should have led to a shift of the second characteristic band toward higher frequencies ($\sim$ 770 cm^{-1}); however, the observed decrease in the frequency of this band (745 cm^{-1}) is possibly a criterion for the absence of a 3,4-structure in the polymer.

Fig. 1

2) In the near IR region (LiF prism), the spectrum of poly-(trans-1-phenylbutadiene-1,3) is identical to that of polystyrene. The close character of these spectra is also found in the region 1600-2000 cm^{-1} (first overtones of $\delta =$ CH) and in the region 1150-1300 cm^{-1}.

3) The bands at 906 and 990 cm^{-1} indicate the presence of vinyl groups, which corresponds to a 1,2-structure (R—CH=CH_2) (approximately 10% relative to trans-olefinic groups).

4) The intense band at 963 cm^{-1}, corresponding to out-of-plane deformation vibrations of = C—H in trans-olefins of the type R—CH=CH—R, indicates the presence of trans-1,4 and trans-3,4 structures. It should be noted that in the spectrum of trans-β-methylstyrene, which contains an element of the

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trans-3,4-structure, and in the spectra of polymers having some amount of trans-3,4-structure (3), a band at 960 cm^{-1} with a shoulder at 980 cm^{-1} is observed. In the spectra of the polymer under study, a shoulder at 980 cm^{-1} is not detected.

This fact, together with what was set forth in point 1, makes it possible to assert that the 3,4-structure is unlikely.

5) The band at 690 cm^{-1}, characteristic of cis-olefinic groupings R—CH=CH—R, coincides with the band of the phenyl group and therefore cannot be used to judge the presence of the indicated structure in the polymer. If, however, atomic models of the polymer are considered, it turns out that the formation of a cis-1,4-structure is unlikely owing to large steric hindrances.
6) Addition of the "head-to-head" type, evidence for which would be the presence of a weak band corresponding to $-CH_2-CH_2-$ groups in the region of 750 cm^{-1}, also cannot be detected because of the very strong band of the phenyl group (745 cm^{-1}).
7) The character of the spectra in the NaCl and LiF regions indicates the complete absence of oxidation products containing the groups $C = O$, $C - OH$, and $C - O - C$.

X-ray analysis of polyphenylbutadiene obtained in heptane shows that the polymer contains a crystalline fraction. This is apparently due to the presence, over fairly long chains, of a regular sequence both in the configuration of the (trans) double bond and in the spatial configuration of the asymmetric carbon atoms. As is known, such polymers are called ditactic (4).

1,4-Polymers of 1-phenylbutadiene-1,3 are of special interest, since they contain truly asymmetric carbon atoms, $= CH - CH - CH_2 -$, if one considers their nearest environment. Therefore

$$\begin{array}{r} | \\ C_6H_5 \end{array}$$

one may expect that every isotactic macromolecule, or any sequence of isotactic monomer units, should possess optical activity.

At present we are continuing studies on the structure of polymers of trans-1-phenylbutadiene-1,3, and also studying the polymerization of this monomer on asymmetric catalysts.

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