*Studies of the Configuration and Conformation of Vinyl-type Polymers. III. The Temperature Dependence of the Infrared Spectra of 2,4-Dichloropentane as a Model Compound of Polyvinyl Chloride**

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In a previous study[1] of the temperature dependence of the infrared spectra of polyvinyl chloride (PVC) in cyclohexanone solution, we found that the intensity ratio of the 696 cm^{-1} band to the 616 cm^{-1} band depends on the temperature, and that this temperature dependence increases with an increase in the syndiotactic configuration of the PVC chain. The temperature dependence has been interpreted as being due to the energy differences among the conformational isomers in the syndiotactic sequences of the PVC chain. Recently, Germar et al. have made a similar study of PVC using the CH_2 bending bands[2] at 1428 and 1432 cm^{-1} and the C–Cl stretching bands[3] near 600∼700 cm^{-1}, and have determined its syndiotacticity.

Shimanouchi and Tasumi,[4] however, have studied the infrared spectra of *meso*- and *dl*-2, 4-dichloropentanes as a model compound of PVC and have suggested that the *dl*-compound, which has the same configuration as the syndiotactic PVC, exists only in one stable conformation in which the C–C chain takes the extended T-T form. This suggests that the syndiotactic sequence in PVC might have the only stable conformation in solution; if so, our previons explanation would be invalid, as well as the explanation by Germar et al.

In order to obtain further information on this problem, we have studied the infrared spectra of the *moso*- and *dl*-compounds in various physical states.

Experimental

2, 4-Dichloropentane was prepared from acetylacetone; 2, 4-pentanediol was prepared[5] by the catalytic hydrogenation of acetylacetone with Raney nickel in an autoclave (H_2 pressure: 125 atm.; reaction temperature: 115∼125°C; reaction time: 150 min.), and it was converted to 2, 4-dichloropentane by reaction with thionylcloride.[6] The boiling point range of the product was 142∼144°C. For the separation of the *meso*- and *dl*-compounds, a Beckman Megachrom preparative gas chromatograph has been used. The purity of the separated compound was certified by infrared inspection.

A Hitachi EPI-2-type double-beam spectrophotometer equipped with a KBr prism was used for the measurement of the infrared spectra. The observation of the solution spectra and their temperature dependence was carried out by using a closed-type cell mounted in a heating device. In order to aid the compensation of absorptions caused by the solvent, a variable-thickness-type cell was inserted in the path of the reference beam. The absorption spectra in a gaseous state were observed with a gas cell 7 cm. in optical path length and with a heating device.

The absorption spectrum in the region of the C–Cl stretching vibrations, which is sensitive to the conformational changes, was also examined.

Results and Discussion

The infrared spectra of the *meso*- and *dl*-compounds in the cyclohexanone solutions at room temperatures are shown in Fig. 1. The results are very similar to the infrared spectra of the pure liquids observed by Shimanouchi and Tasumi;[4] the *meso*-compound has two absorption bands at 683 and 616 cm^{-1}, and the *dl*-compound also has two absorption bands at 629 and 607 cm^{-1}. On the basis of the empirical rules concerning the relation between the frequencies of the C–Cl stretching bands of some chlorohydrocarbons and their geometrical conformations, Shimanouchi and Tasumi[4] have concluded that the *dl*-compound has only one stable conformation in which the C–C chain takes the T-T conformation, and that the *meso*-compound is stable in the conformation of the T-G or G′-T with respect to the C–C

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[5] M. Shiraki and H. Nagai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 976 (1960).

[6] S. Okumura, "Jikken Yuki Kagaku" (Experiment in Organic Chemistry), I, Kyōritsu-Shuppan, Tokyo (1953), p. 158.

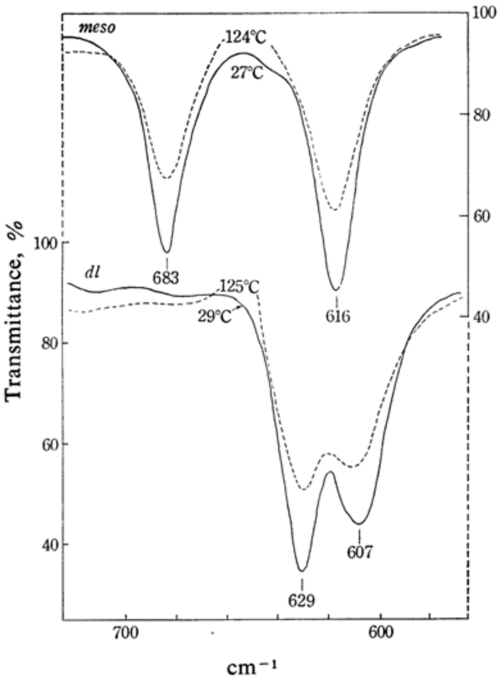
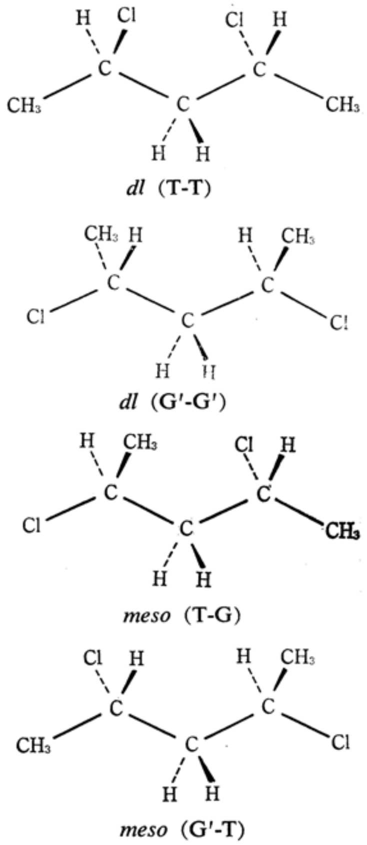


Fig. 1. The infrared spectra of the *meso*- and the *dl*-compounds in a cyclohexanone solution at the various temperatures.

main chain, as Fig. 2 shows. Since the T-G conformation is a mirror-image of the G′-T conformation, both conformations should give the same spectra. The observed infrared spectra of the *dl*- and the *meso*-compounds in the cyclohexanone solutions are caused by the structures of the T-T and the T-G or G′-T conformations respectively.

The purpose of this investigation is to investigate the possible existence of the other species of the rotational isomer of both compounds in a cyclohexanone solution at higher temperatures. Especially, the G′-G′ conformation for the *dl*-compound may be expected to appear in the solution at higher temperatures, because the potential energy of the G′-G′ conformation would be the next lowest after that of the T-T conformation.[3,8]

However, the infrared spectra of both the *dl*- and the *meso*-compounds in solution at a temperature near 120°C are identical with the respective spectra at room temperature, as is shown in Fig. 1. In the gaseous state, none of the new bands which could be expected from the new conformational isomers other than the T-T conformation in the *dl*-compound can be observed, even in the higher temperatures near 170°C. For the *meso*-compound, in the gaseous state the infrared spectrum at 164°C does not differ from that at room temperature. These results are shown in Fig. 3.



dl (T-T)

dl (G′-G′)

meso (T-G)

meso (G′-T)

Fig. 2. The probable conformations in the *meso*- and the *dl*-compounds.

These facts show that the G′-G′ conformation in the *dl*-compound may be rejected because the band centered near 690 cm⁻¹, which is expected from the stretching vibration of the C–Cl bond trans to the adjacent C–C bond in the G′-G′ conformation, does not appear in the spectra of the *dl*-compound. Thus, it may be concluded that the sole structure which is stable in the *dl*-compound in the cyclohexanone solution is the structure of the T-T extended conformation in the temperature range of this investigation, as in the previous examination of the solution spectra of PVC. For the *meso*-compound, no stable structures other than the T-G or G′-T conformation could be found in the same temperature range. Consequently, it is impossible to explain the temperature dependence of the intensities of the C–Cl stretching bands of the solution spectra of PVC as being due to the rotational isomerism of the polymer chain so long as 2,4-dichloropentanes are applied as model compounds of PVC.

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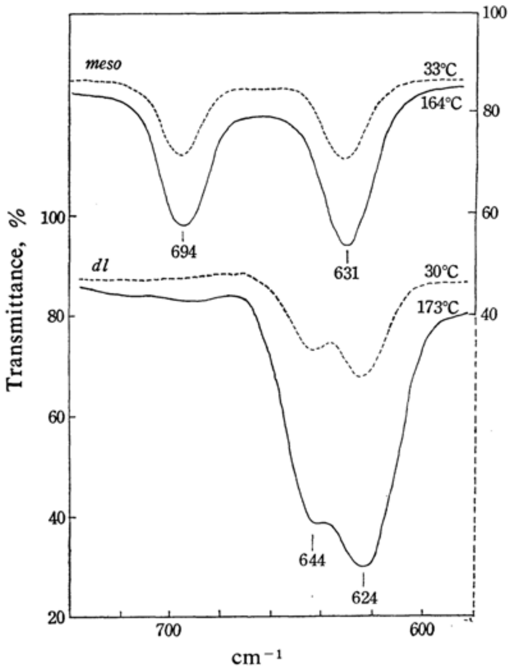

Fig. 3. The infrared spectra of the *meso*- and the *dl*-compounds in the gaseous state at the various temperatures.

In order to obtain further information on the temperature dependence of the intensities of the C–Cl stretching bands of PVC, the infrared spectra of a mixture of 1 cc. of the *meso*-compound and 2.4 cc. of the *dl*-compound (a model of 70% syndiotactic PVC) was investigated in the cyclohexanone solution. In the spectrum of the mixture, the highest frequency and the second highest frequency are caused by the *meso*- and *dl*-compounds respectively. The band at 616 cm^{-1} of the *meso*-compound and the band at 607 cm^{-1} of the *dl*-compound are superposed on the band centered to 612 cm^{-1}. As is shown in Fig. 4, the intensity ratio, D_{612}/D_{683}, of the mixture depends only slightly on the temperature, while the corresponding intensity ratio, D_{616}/D_{696}, of PVC depends strongly on the temperature. In the case of the isolated compound, the relative intensity of the two C–Cl stretching bands of the *meso*-compound only slighty depends on the temperature. However, that of the *dl*-compound shows a remarkable dependence on temperature, as Fig. 5 shows. The change in the intensity ratio D_{612}/D_{683} in the solution spectra of the mixture with heating is dut to the contribution from the temperature effect on the intensities of the absorption bands of the *dl*-component. However, the reason why the greater temperature effect can be found in the *dl*-compound can not be determined.

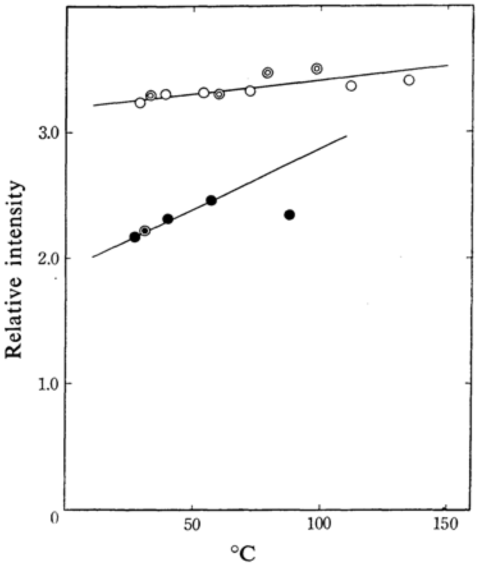

Fig. 4. The temperature dependence of the relative intensities of the C–Cl stretching bands of the *dl-meso* mixture and of the syndiotactic PVC (polymerized at −60°C) in cyclohexanone solutions. The double circles denote the observed points obtained on cooling.

-○- D_{612}/D_{683}, *dl-meso* mixture (*dl* 70%)
-●- D_{616}/D_{696}, PVC polymerized at −60°C

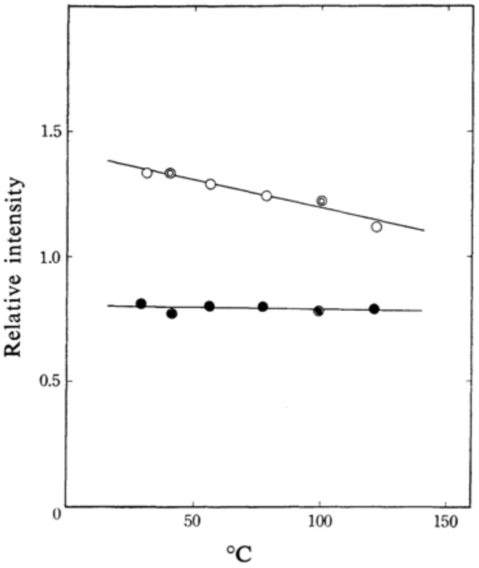

Fig. 5. The temperature dependence of the relative intensities of the two C–Cl stretching bands in the *dl*- and the *meso*-compounds in cyclohexanone solutions. The double circles; as for Fig. 4.

-○- *dl*, D_{629}/D_{607}
-●- *meso*, D_{683}/D_{616}

The remarkable temperature dependence of the solution spectra of PVC may probably be ascribed to the effect of the interchain interaction among the polymers. This speculation is consistent with the result reported by Asahina and Enomoto;⁹⁾ in a cyclohexanone solution, the intensity of the 648 cm^{-1} band of PVC has a tendency to decrease with the concentration decrease of the syndiotacticity. In a rather concentrated solution, it seems likely that the longer syndiotactic sequences of the polymer chain lie in a quasi-crystalline state, in which the conformation of the polymer chain may be in the extended T-T form. As Fig. 6 shows, this is confirmed by the fact that, in the solution spectra, the intensity of the 648 cm^{-1} band to which the crystalline syndiotactic parts contribute¹⁰⁾ becomes stronger as the polymerization temperature of the polymer is lowered. Figure 7 gives the intensity change with the heating of the C–Cl stretching bands of the syndiotactic PVC (polymerized at −60°C) in the cyclohexanone solution. With an increase in the temperature, the desolvation of the quasi-crystalline parts in the solution occurs and leads to a decrease in the relative intensity ratio, D_{648}/D_{696}, accompanied by an increase in the relative intensity ratio, D_{616}/D_{696}. In the later intensity ratio, the 616 cm^{-1} band has been assigned to the amorphous syndiotactic part.¹⁰⁾

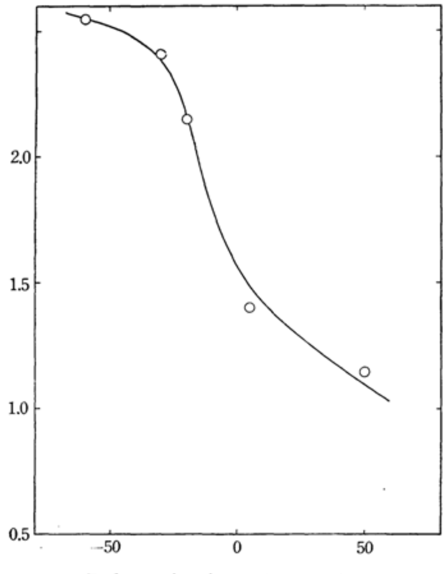

Fig. 6. The relation between the relative intensities of the C–Cl stretching bands of PVCs in cyclohexanone solutions at 30∼35°C, against the polymerization temperature of the polymers. -○- D_{648}/D_{696}

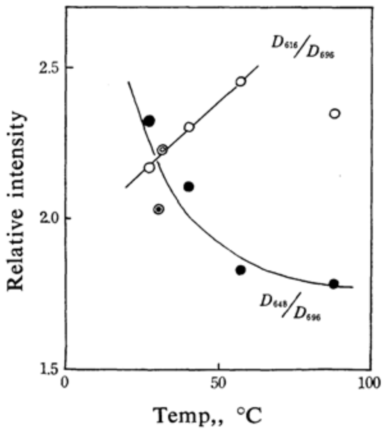

Fig. 7. The temperature dependence of the relative intensities of the C–Cl stretching bands of the syndiotactic PVC (polymerized at −60°C) in a cyclohexanone solution. The double circles; as for Fig. 4.

In the light of the above experimental results, we have come to the following conclusions. Firstly, if the C–Cl stretching bands fall in different frequency regions depending on the two substituents which are trans to the Cl atom across the two adjacent C–C bonds, as has been pointed out by Krimm,¹¹⁾ a compound which at least consists of the three monomeric units of PVC must be employed as a model compound of PVC. Secondly, the temperature dependence of the absorption intensity in the spectra of PVC cannot be directly related to the rotational isomerism of the polymer chain. Moreover, the intensity of the C–Cl stretching bands of the syndiotactic and the isotactic sequences of PVC may be differently affected by the temperature.

In addition to the results given by us¹⁾ and Germar³⁾, such a temperature effect on the intensity of the C–Cl stretching band and the effect of the interchain interactions among the polymers must be taken into account in the interpretation of the temperature dependence on the infrared spectra of PVC.

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