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Infrared spectral study of diphenylether polymers

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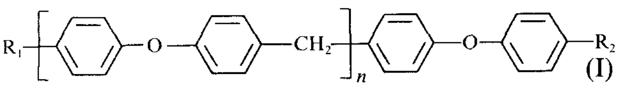
Infrared spectra of polymer, obtained by condensation of diphenylether with formaldehyde in sulphuric acid–alcohol medium are studied. Conclusions about the structure of the oligomer and the thermally treated products are made. A quantitative method for studying the dependence of the kinetics of polycondensation on the temperature and the quantity of the catalyst $SnCl_4$, is developed.

1. Introduction

Diphenylether polymers (DPE) exhibit high thermal stability, good mechanical properties, chemical and water resistance [1]. Due to these good characteristics, simplified methods for preparation of the initial reactive DPE derivatives are developed and optimal coating techniques are found [2]. Preparation of DPE–ethoxymethylene derivatives by condensation of DPE with formaldehyde in sulphuric acid–alcohol medium was described previously [3]. The reaction product is a mixture of oligomers with the suggested formula:



(I)

where R_1 = H or $CH_2O-C_2H_5$; R_2 = $CH_2OC_2H_5$; n = 0 to 1.

A highly viscous precondensate soluble in organic solvents is obtained when heating the reaction mixture in the presence of $SnCl_4$. A crosslinked oligomer is prepared when additional quantities of $SnCl_4$ were added to the resulting precondensate, it was then heated at high temperatures.

The present paper is concerned with the results of an infrared study on DPE–ethoxymethylated product. The results are in good agreement with literature data and this gave us the opportunity to make some assumptions about the structure of the oligomer and the obtained coating after thermal treatment. A technique for quantitative determination of ethoxymethylene groups is developed. The dependence of the kinetics of polycondensation on temperature and catalyst is studied by this technique.

2. Experiments

The preparation of initial DEP oligomer was described earlier [3]. Precondensation is carried out at 140° C in the presence of 0.3 wt % $SnCl_4$ as a 10% solution in dichlorethane. Kinetic studies are carried out on films obtained by evaporation of 50% toluene solution of precondensate in the presence of 1 wt % $SnCl_4$ catalyst. The solution is poured on to a potassium bromide disc, diameter = 12 mm, and pressed by the standard method. The test samples are subjected to infrared quantitative spectral analysis. The initial DPE, the reaction fractions and precondensate are photometered as a capillary layer between the sodium chloride windows.

The infrared spectra are obtained using UR-10 Carl Zeiss Jena Spectrophotometer (2000 to 650 cm^{-1}, NaCl prism; 3700 to 2000 cm^{-1}, LiF prism). Quantitative measurements are carried out in the basic line method. Data in Figs 4 and 5 are the averaged values of three measurements. The error of the averaged value is ±2.5%.

3. Results and discussion

The infrared spectra of DPE oligomer and the initial DPE are shown in Fig. 1. Comparing the two spectral curves the following conclusions may be drawn:

1. Bands at 765 and 695 cm^{-1} are observed in the infrared spectra of DPE oligomer. They are typical for the monosubstituted benzene ring. This confirms the suggested Formula I. Indicated absorption maxima do not belong to the free DPE, because the test sample is taken from the reaction mixture in the temperature range 290 to 320° C.

2. The appearance of a new band at 1100 cm^{-1} ($\nu_{C-O-Alk}$) suggests the presence of ethoxymethylenic groups in the resultant oligomer. Typical CH_2- and CH_3- valence frequencies in the region 3000 to 2800 cm^{-1} confirm the aforementioned conclusion.

3. The band between 850 and 820 cm^{-1}, which is absent in the spectrum of DPE, corresponds to the CH- out of plain deformation vibrations in the 1,4- or 1,2,4 (1,3,4)-substituted benzene ring. The formation of linear or branched chains in the oligomer molecule is a very interesting problem because it directly relates

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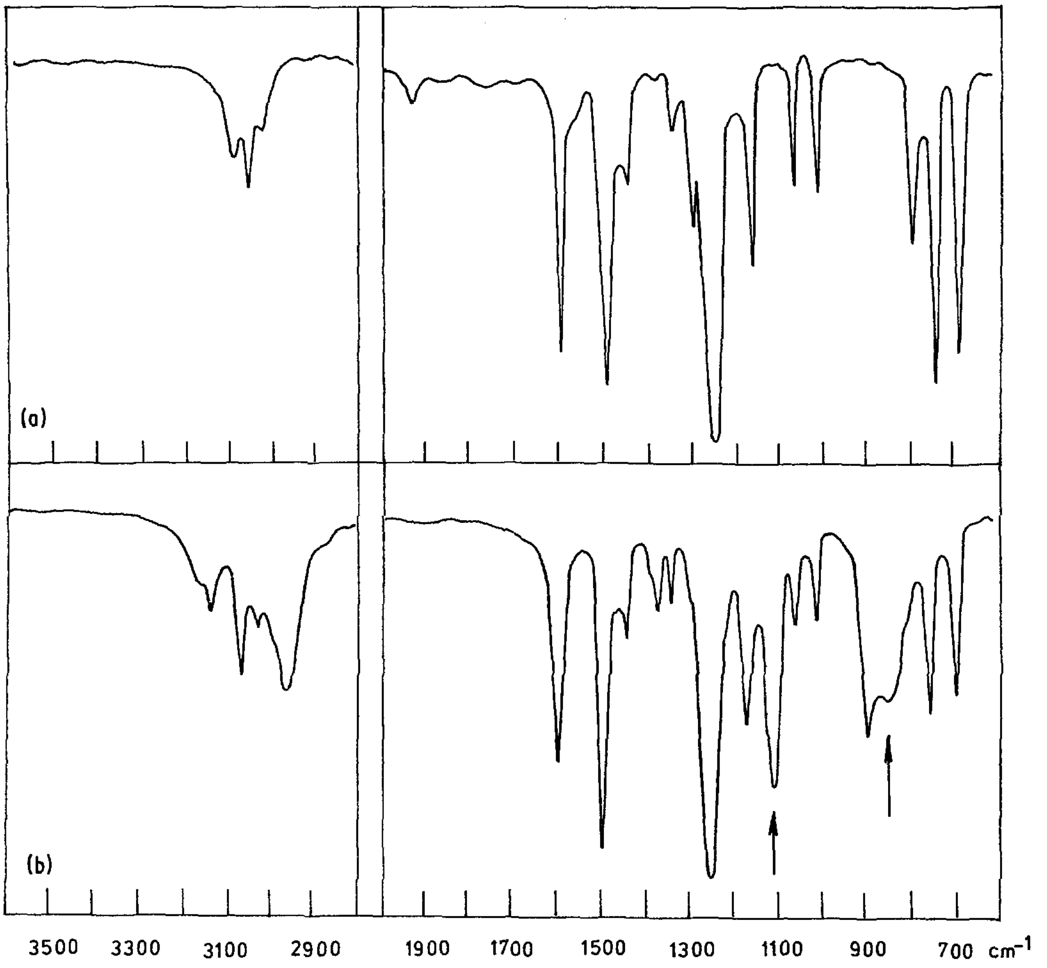

Figure 1 Infrared spectra of (a) DPE; (b) fraction of the reaction mixture at 290 to 320° C.

to the mechanism of crosslinking of the coatings. We tried to solve this problem by comparing experimental results with those given in [4] and [5] for infrared spectra of model compounds from the type (I), where R_1 = CH_2OH, $CH_2COOC_2H_5$, $C_6H_4NO_2$; R_2 = H, CH_2OH: n = 1 or 2. The spectral curves are very similar in the region 950 to 650 cm^{-1}. For example, in Fig. 2, DPE oligomer and *p,p'*-diphenoxydiphenylmethane (I: R_1 = $CH_2COOC_2H_5$; R_2 = H; *n* = 1) spectra are shown in the same region. Since the discussed spectral region is very specific for this type of substitution, the above result confirms the linear structure (I) of the DPE oligomer.

Infrared spectra of coatings before and after treatment are compared in Fig. 3. Spectra of the oligomer and of the prepolymer are very similar (see Figs 1 and 3a). This result demonstrates that the precondensation is mainly connected with the lengthening of the linear chain.

The intensity of the bands at 695, 765, 850 and 1100 cm^{-1} sharply decreases after curing the test sample (Fig. 3b). This phenomenon can be explained by exhausting mono- and disubstituted benzene rings and ethoxymethylene groups in the process of crosslinking. A new band appears at 930 cm^{-1} corresponding to the tetra- and penta-substituted aromatic rings.

The absorption maxima remain constant at 1250 and 1180 cm^{-1} $\nu_{(C-O-Ar)}$, which means that polycondensation

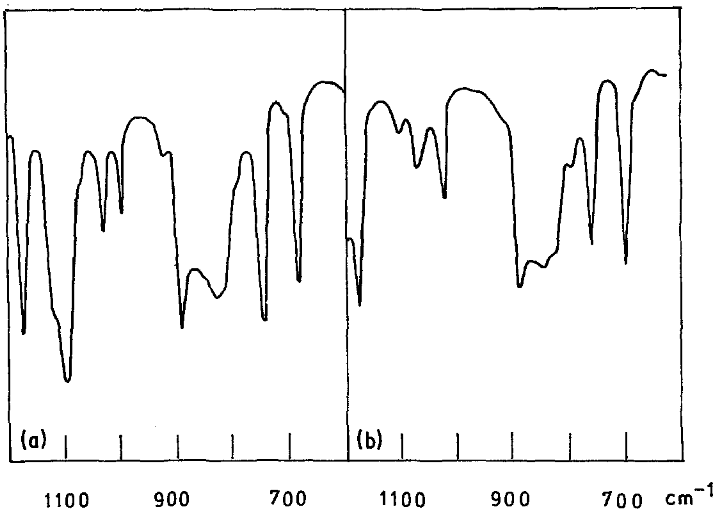

Figure 2 Infrared spectra in the region 1200 to 650 cm^{-1} of (a) DPE oligomer; (b) *p*-propionate of *p,p'*-diphenoxydiphenylmethane.

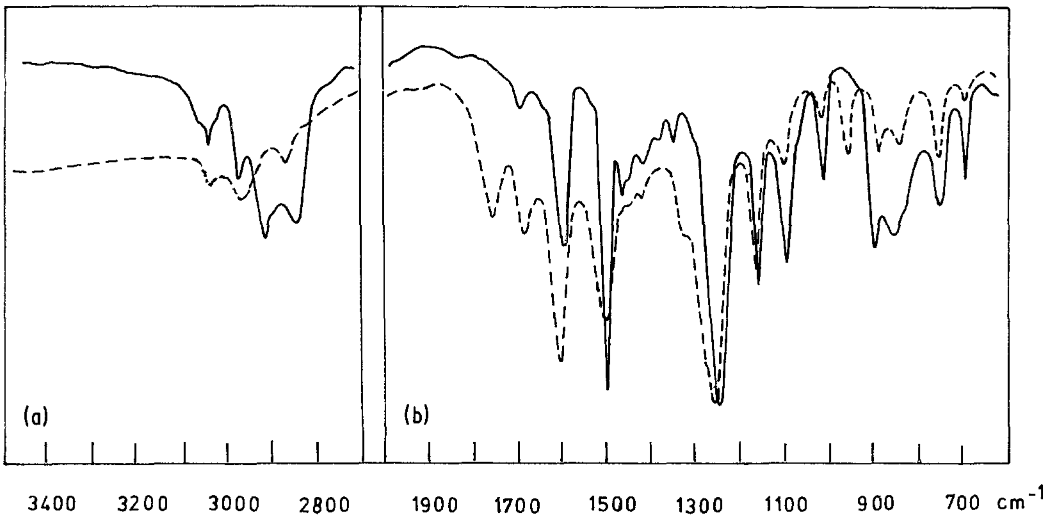

Figure 3 Infrared-spectra of (a) freshly applied coating (———), (b) thermally treated coating at 250° C for 18 h (– – –).

does not influence the content of diphenylether units. The two new bands in the region 1740 to 1680 cm^{-1} correspond to the valence frequencies of C=O bonds. These new bands appear after prolonged curing at temperatures over 200° C. This was established by comparison of the infrared spectra for every stage of polycondensation. The curves of isothermal ageing confirmed the presence of oxidative products: at the beginning of the curves an increase of polymer weight is noticed which is due to the oxygen absorption and then a subsequent oxidation destruction is observed.

If we assume that the polymer is obtained by the binding of ethoxymethylene groups, then a direct relationship will exist between the degree of polymerization and the absorbance (A) of the band at 1100 cm^{-1}. Therefore, the variations of A^{1100} will give information about the relationship between the kinetics of polymerization and the temperature or the catalyst content.

The ratio method is used in quantity studies, since a reproducible thickness of the coating cannot be prepared. As the band intensity at 1180 cm^{-1} is constant (Ar–O–Ar bond content is constant in crosslinking) the Lambert – Beer law is used:

$$A^{1100} = a^{1100} b c_{\mathrm{CH_2OC_2H_5}} \qquad (1)$$

and

$$A^{1180} = a^{1180} b c_{\mathrm{Ar\text{–}O\text{–}Ar}} \qquad (2)$$

where A^{1100} and A^{1180} are the absorbances of corresponding bands at 1100 and 1180 cm^{-1}, and a^{1100} and a^{1180} are the absorption coefficients, b is the thickness of the layer, $c_{\mathrm{CH_2OC_2H_5}}$ and $c_{\mathrm{Ar\text{–}O\text{–}Ar}}$ are the concentrations of ethoxymethylenic and diphenylether units, respectively.

The ratio:

$$R = \frac{A^{1100}}{A^{1180}} = \text{constant} \times c_{\mathrm{CH_2OC_2H_5}} \qquad (3)$$

is independent of the layer thickness b, and it is in direct proportion to the concentration of $\mathrm{CH_2OC_2H_5}$ bonds, because a^{1100}, a^{1180} and $c_{\mathrm{Ar\text{–}O\text{–}Ar}}$ are constant.

The assumption that $c_{\mathrm{Ar\text{–}O\text{–}Ar}}$ does not change in the crosslinking is proved experimentally: the absorption at 1180 cm^{-1} is studied compared to the time of thermal treating (Table I). Resulting data are independent of curing time in the error limits of the method.

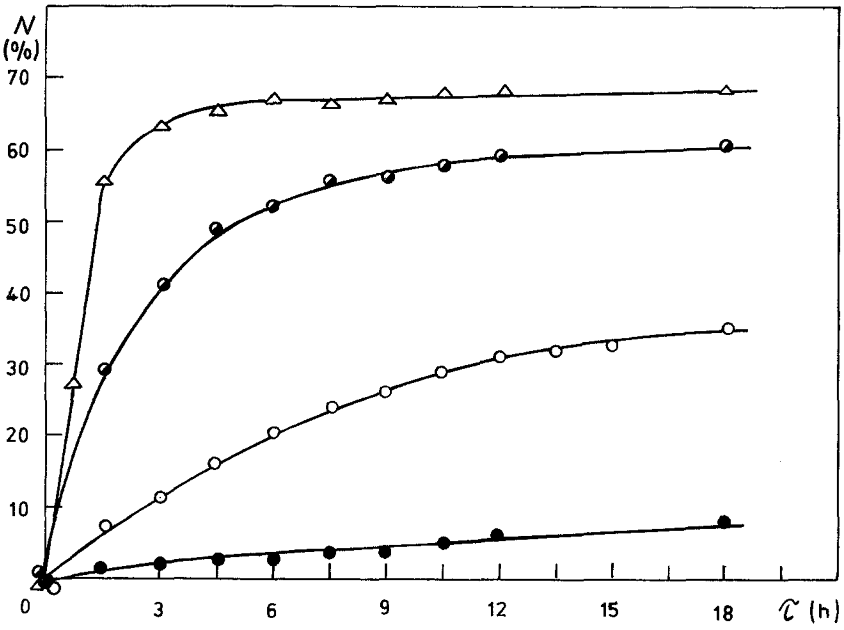

Figure 4 Kinetic curves: degree of polycondensation against temperature. ● 130° C, ○ 160° C, ◑ 190° C, △ 220° C.

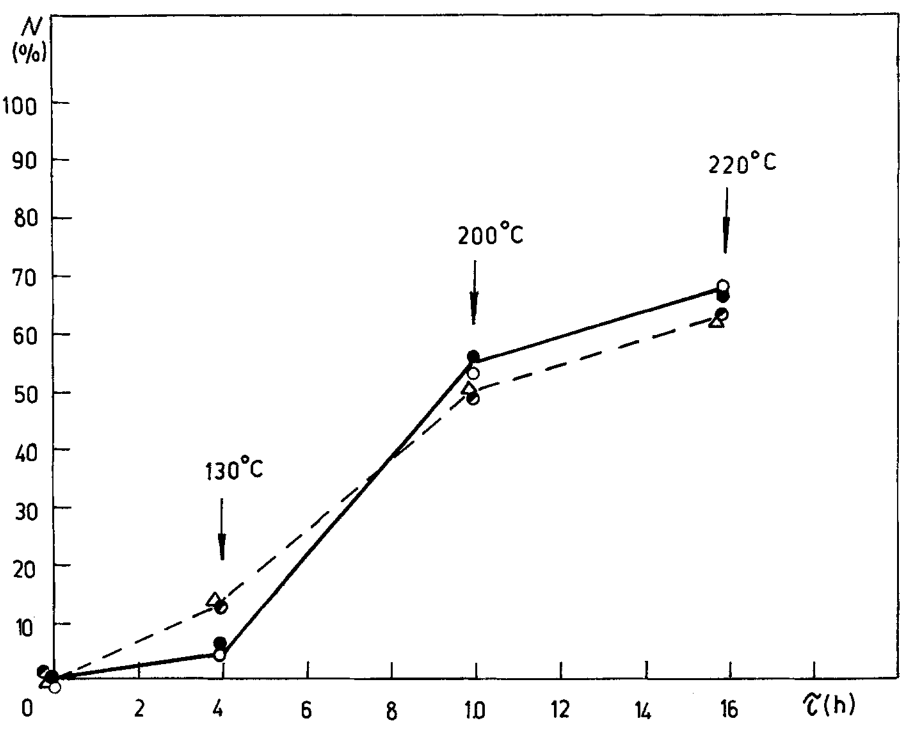

Figure 5 Relationship between the degree of polycondensation and the quantity of the catalyst. -●- 0.3% $SnCl_4$, -○- 1.0% $SnCl_4$; --◐-- 3.0% $SnCl_4$, --△-- 5.0% $SnCl_4$.

The kinetic curves at 130, 160, 190 and 220° C are given in Fig. 4, where $N\% = [(R_0 - R)/R_0] \times 100$ characterizes the degree of polycondensation. It is evident that the saturated value of N is not reached at temperatures of 130 and 160° C for 18 h. The kinetic curve at 190° C shows saturation after 12 h thermal treatment, but $N_{\text{satur.}}$ is 8 to 10% lower than those at 220° C. The two curves do not tend to cross. A saturation occurs at 220° C for 5 to 6 h which is in agreement with experimentally established technological conditions (leaflet from Mitsubishi Denki Japan). It is established that the polymerization is finished after thermal treatment at 250° C for 18 h. At higher temperatures oxidation occurs (Fig. 3b).

The measured equilibrium values show that free ethoxymethylene groups were present in the reaction mixture after the process of crosslinking. In fact, the relative maximum degree of polymerization of 70% corresponds to 3% free alkoxy groups in relation to the total weight of original oligomer. This result is in agreement with the other published results on polycondensation of resol resins. This phenomenon could be explained by the steric hindrance of the reaction nucleus in forming the polymer network.

Fig. 5 shows the effect of the catalyst quantity on the kinetics of polymerization. According to [6], the optimal quantity of $SnCl_4$ is in the range 0.8 to 2 wt %. We found that 0.3 wt % is sufficient quantity to reach the maximum degree of crosslinking. Additional proof that maximum crosslinking is reached at 220° C is obtained by comparing N values at 200 and 220° C (Fig. 5).

TABLE I The relationship between A^{1180} and the time of thermal treatment at 220° C

τ (h)	A^{1180}
0.0	0.23
1.5	0.23
3.0	0.23
4.5	0.23
6.0	0.24
7.5	0.23
9.0	0.24
10.5	0.24
12.0	0.24

4. Conclusions

The results from the infrared spectral study can be summarized as follows:

1. According to the cited literature the structure of the DPE oligomer and the densified prepolymer is mainly linear.
2. The infrared spectral analysis of the thermally treated products shows that the crosslinking is completed by binding the ethoxymethylene groups with benzene rings from the linear chain.
3. The quantity method for studying the effect of temperature on the kinetics of polycondensation is developed. It is found that the optimal curing temperature of the coating is 220° C for 5 to 6 h.
4. The infrared spectral quantity method proved that 0.3 wt % $SnCl_4$ is sufficient to catalyse the polymerization.

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