Study of the Oligoester Maleinates Containing an Isocyanuric Ring by Infrared Spectroscopy

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Synopsis

Processes taking place in crosslinked oligoester maleinates containing an isocyanuric ring were studied by means of infrared and ESR spectroscopy and heating from 110° to 600°C. By determining the optical density of the carbonyl groups at 1690 cm^{-1}, of the CH$_2$— groups at 1460 cm^{-1}, ether and ester groups at 1120 and 1260 cm^{-1}, and vinyl groups at 935 and 990 cm^{-1}, their mutation by hardening and tempering of the polymers was followed. The investigation shows that the carbonyl absorption of the oligoester maleinates containing an isocyanuric ring is double and that of the oligoester propyleneglycol maleinate phthalate is single. By modification of the isocyanuric oligoester maleinates with phthalic, adipic, sebacic, and other acids, an increase of the speed of isomerization of maleic groupings to fumaric is observed. By building of isocyanuric links in oligoester maleinates, a more stable structure is obtained. Above 330°C, isocyanuric links probably regroup into polycyanic links. The typical carbonyl absorption precipitously decreases at 400°C and disappears altogether at 600°C. On the basis of the investigations carried out, it is assumed that, in the process of hardening and thermodestruction of the polymers investigated, and radical processes obviously play an essential part

INTRODUCTION

We have reported[1,2] the synthesis of oligoester maleinates containing an isocyanuric ring and allyl groups which, on the basis of elemental analysis and IR spectra can be schematically presented by the following formula:

I

where R = H;   (phthalic ring)   ; —OC(CH$_2$)$_4$CO—; —OC(CH$_2$)$_8$CO—; etc.

$x = 1$ $x = 0,5$

$y = 1$ $y = 0,5$

937
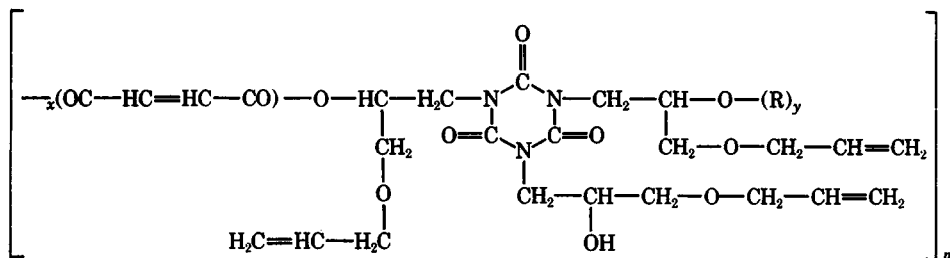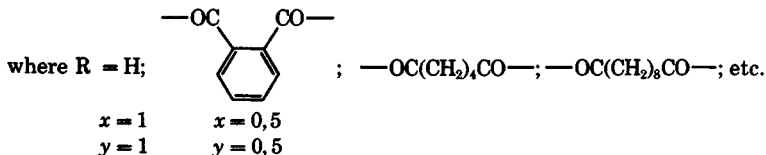
By means of radical copolymerization of the oligoester maleinates thus obtained with styrene in the presence of peroxide initiating agents, they are transformed to crosslinked polymers. Only some of the results obtained from the IR and ESR spectroscopic investigation of the chemical processes taking place during hardening and destruction of the oligoester maleinates containing an isocyanuric ring by heating to 600°C are considered in this report.

EXPERIMENTAL

Four kinds of isocyanuric oligoester maleinates were synthetized for the purpose of investigation (compound I). By mixing these oligoester maleinates with 50% styrene and 1.5% benzoyl peroxide under identical conditions (29 hr at 60°C, 25 hr at 90°C, and 2 hr at 110°C), corresponding crosslinked polymers were obtained, which we designated as follows: allylisocyanuric polyester maleinate (ALICPE-M), allylisocyanuric polyester maleinate phthalate (ALICPE-MPh), allylisocyanuric polyester maleinate adipate (ALICPE-MA), and allylisocyanuric polyester maleinate sebacate (ALICPE-MS). Under identical conditions crosslinked polymer is obtained by means of polymerization of common oligoester maleinate synthetized of propyleneglycol and maleinic and phthalic anhydride, which we designated as PPE-MPh. Infrared spectra were produced on the hardened oligoester maleinates before and after tempering in a thermostat for 3 hr at 150°, 180°, 250°, and 300°C and for 1 hr at 400°, 500°, and 600°C by a Unicam Sp-200 spectrograph in a region of 650 to 4000 cm^{-1}. The patterns are in the form of pellets of potassium bromide (30 mg of a pattern to 2 g of potassium bromide).

IR spectra of films of the initial oligoester maleinates were produced for comparison.

On the basis of the IR spectra obtained, the mutation was quantitatively followed of carbonyl groups, CH_2— groups, ethers and ester groups, and double bonds during hardening at 110°C; and of the polymers tempered at 150°, 180°, 250°, and 300°C by means of determining the optical density of carbonyl groups at 1690 cm^{-1}, CH_2— groups at 1460 cm^{-1}, the valence vibration of C—O groups at 1260 and 1120 cm^{-1}, CH_2=CH— and OH in COOH at 935 cm^{-1}, and CH_2=CH— and —CH=CH— at 990 cm^{-1}. As inner standard an absorption band of the isocyanuric ring at 765 cm^{-1} was used for ALICPE-M, ALICPE-MPh, ALICPE-MA, and ALICPE-MS; and a band of the aromatic ring at 700 cm^{-1} was used for PPE-MPh, which by polymerization and tempering at 300°C do not undergo mutation. Calculations were made according to the combined law of Buge-Lambert-Beer, and the following formulas were used:

$$D_1 = \lg \frac{I_0}{I}$$

$$D_2 = \lg \frac{I_0}{I}$$

where D_1 = optical density of the polymer investigated; D_2 = optical density of the standard used; I_0 = intensity of incident light upon the polymer investigated; and I = intensity of light passed through the polymer investigated. ESR spectra were obtained on a Japanese apparatus IES-3-BS-X, and DPPHC (1,1'-diphenyl-2-pycrinehydrazine) was used as reference material.

RESULTS AND DISCUSSION

The IR spectra of some of the polymers studied are plotted in Figures 1 and 2. (The IR spectra of ALICPE-MPh, ALICPE-MA, and ALICPE-MS are not plotted. We observed the same typical absorption of C=O, C—O,
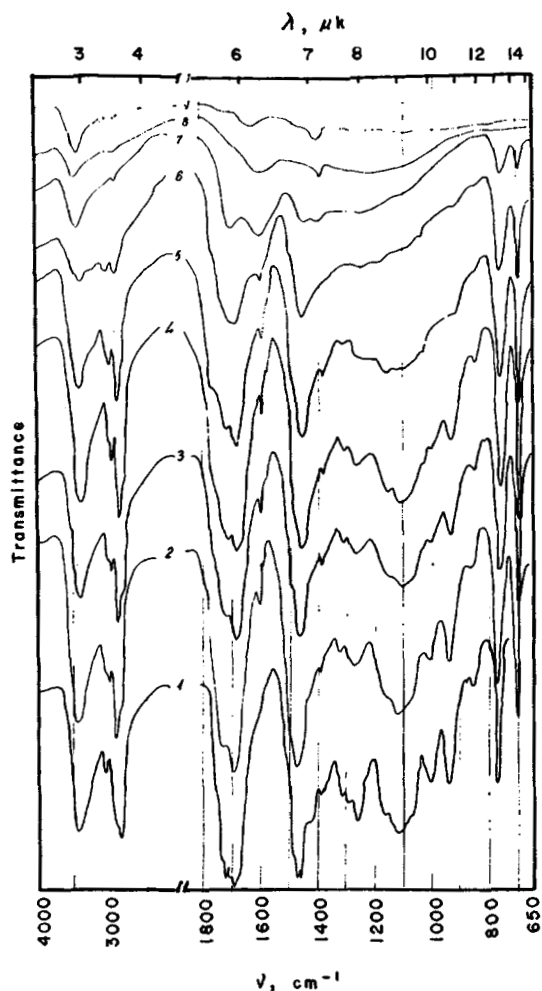

Fig. 1. Infrared spectra of ALICPE-M: (1) initial; (2) 110°; (3) 150°; (4) 180°; (5) 250°; (6) 300°; (7) 400°; (8) 500°; (9) 600°C.

CH$_2$=CH—, —CH=CH—, and other groups, which differ only in their intensity.)

The shapes of the curves show that the IR spectra of the polymers studied are very complex, and for a simple interpretation of some of the bands a special study was necessary. The IR spectra can be interpreted as follows: The frequency interval at 3520–3400 cm^{-1} corresponds to the valency vibration of the OH group. The shapes of the spectra show that, by hardening the polymers at a higher temperature, the intensity of the absorption band decreases, but it is preserved at 600°C. At 2940 and 2850 cm^{-1}, the absorption bands appear as a result of the valency symmetrical and asymmetrical vibration in CH$_2$— and CH$_3$— groups.[3] By heating to a higher
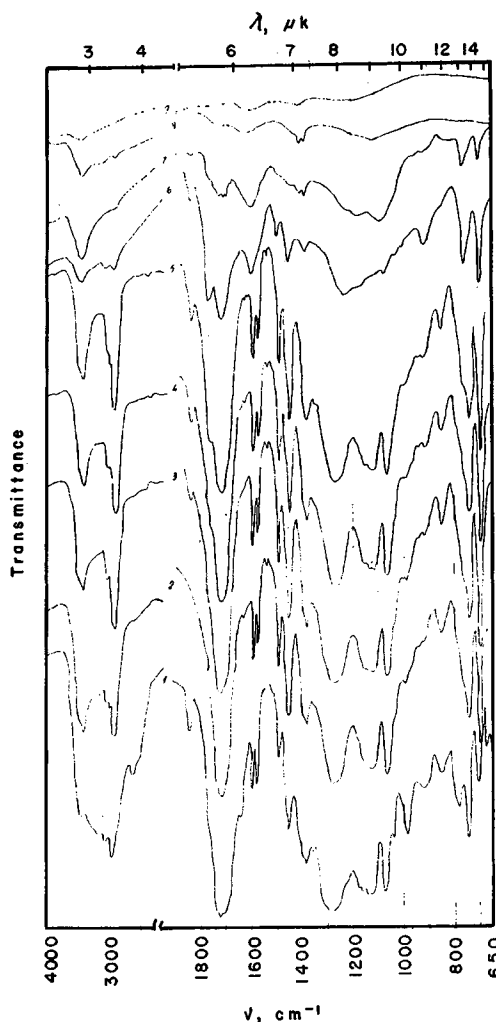

Fig. 2. Infrared spectra of PPE-MPh: (1) initial; (2) 110°; (3) 150°; (4) 180°; (5) 250°; (6) 300°; (7) 400°; (8) 500°; (9) 600°C.
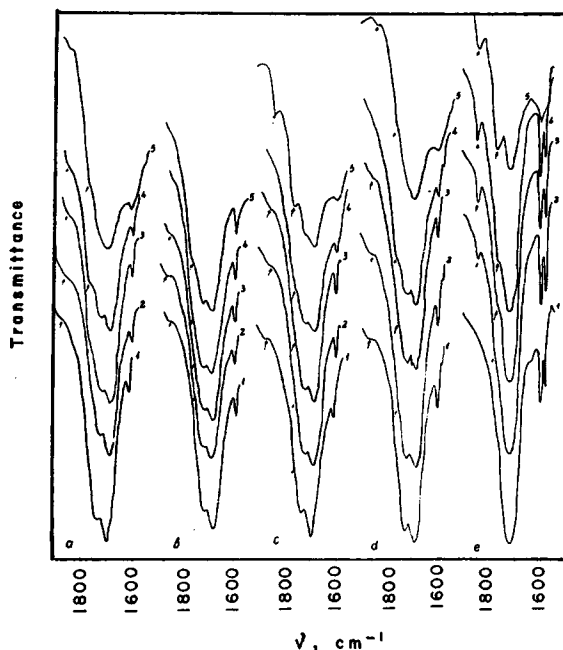
Fig. 3. Infrared spectra of polymers: (a) ALICEP-M; (b) ALICPE-MPh; (c) ALICPE-MA; (d) ALICPE-MS; (e) PPE-MPh; (1) 110°; (2) 150°; (3) 180°; (4) 250°; (5) 300°C.

temperature these bands decrease, and at 500° and 600°C they are very weak in ALICPE-M, ALICPE-MPh, ALICPE-MA, and ALICPE-MS, and disappear in PPE-MPh.

The IR spectra of the oligoester maleinates consist of vibrations of the aliphatic part of the molecule (—CH₂, —CH₃, and other groups) and a vibration localized in the carboxyl group.[4]

The principal characteristics of the carboxyl group consist of several characteristic vibrations: (a) the valency vibration of OH; (b) the valency vibration of C=O; (c) the valency vibration of C—O; (d) the deformation vibration of angle —C⟨^{O}⟩H, etc.; (e) deformation vibration of C=O by cis or trans forms (maleinic or fumaric acids).[2,5]

The appearance of an absorption band at 1770 cm⁻¹ is probably related to the formation of five atomic cycles in the structures of the polymers (Fig. 3).

The possibility of formation of six atomic cycles is not excluded, provided their characteristic absorptions and the absorption of the maleinate acid links cover each other. The realization of cyclization depends on a number of factors, the main one being the tension of the cycle formed. On this basis, five- and six-atomic cycles are easily formed.[6] Due to the strong carbonyl absorption of polymers containing isocyanuric links at 1770 cm⁻¹, the bands are in the form of an inflexed shoulder. At higher tempering
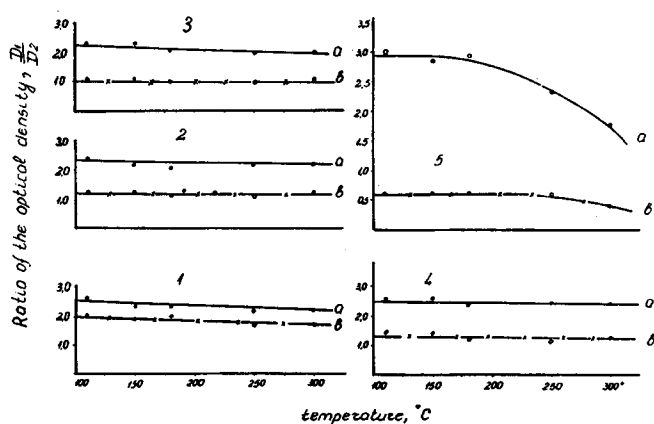
Fig. 4. Change in the ratio of optical densities with temperature: (1) ALICPE-M; (2) ALICPE-MPh; (3) ALICPE-MA; (4) ALICPE-MS; (5) PPE-MPh; (a) D_1 (1690 cm^{-1})/D_2(765 cm^{-1}). (b) D_1(1460 cm^{-1})/D_2(765 cm^{-1}).

temperatures, the latter band is better outlined (Fig. 3a, b, c, and d). This band is best outlined in PPE-MPh (Fig. 3e). The absorption observed at 1840 cm^{-1} (Figs. 2 and 3e) is related to the formation of cycles of greater tension.

The shapes of the curves (Figs. 1 to 3) show that with increase in tempering temperature, the intensity of these bands increases up to 300°C. At a higher temperature, a certain decrease is observed, and at 500°C they disappear. This shows that the cycles obtained remain stable to 350°–400°C. Probably the high thermostability of the polymers investigated indicates the formation of cyclic structures in the basic chain of the polymer structures.[7–9] On the basis of chemical analysis and investigation of the properties of the isocyanuric polymers, we recently reported[9–11] that, side by side with the linear structure, cyclization results from the intermolecular and intramolecular reactions between acids and allylic double bonds. The curves show that the carbonyl absorption of PPE-MPh (Figs. 2 and 3) is single, whereas that of all isocyanuric oligoester maleinates (Figs. 1 to 3) and their crosslinked polymers is double. Taking into consideration some published data[3] and on the basis of the spectra of model mixtures produced by us, it should be assumed that in the latter case the band at 1690 cm^{-1} is due to the isocyanuric and fumaric carbonyl groups, and that bands at 1740–1720 cm^{-1} are due to the carbonyl groups of the maleic and other acidic links. Figures 1 and 2 show that by tempering the polymers investigated at a higher temperature, a decrease in the last band is observed and that at 300°C it disappears. This is a result of the partial and complete isomerization of the maleic to fumaric links during the preparation, hardening, and tempering of the isocyanuric oligoester maleinates.

The shapes of the curves (Fig. 4) show that the ratio of the optical density of the C=O group at 1690 cm^{-1} up to 300°C practically does not change in isocyanuric crosslinked polymers. This shows that with the building of

the isocyanuric links in ologoester maleinates a more stable structure is obtained, which up to 300°C is quite resistant to oxidation and degradation. The effect of stabilization of the polymer structure which we observed confirms the data published on other isocyanuric polymers.[12-14] The curves (Fig. 4) clearly show that, at a temperature above 180°C, a precipitous decrease of the optical density ratio of carbonyl groups in PPE-MPh is observed. This is probably related to the destruction of carboxyl groups. The data show that this process takes place at a higher speed and at a temperature above 300°C, and that at 600°C the characteristic absorption of the C=O group disappears (Fig. 2).

The investigation carried out (Figs. 1 to 3) shows that at temperatures higher than 350°C, the intensity of carbonyl absorption precipitously decreases and practically disappears at 500°C. This is probably related to the destruction of carboxyl groups and similarly to the regrouping of isocyanuric links in a secondary polymer in which nitrogen is bound in the form of polycyanic links.[15-17] This process is obviously accelerated by the formation of free radicals (low-molecular or polymeric) as a result of destruction. They join the isocyanuric ring with subsequent opening of the ring according to the following reaction:
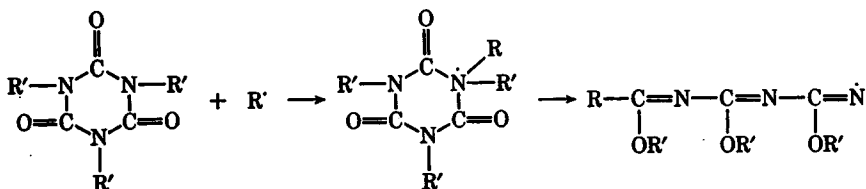
As a result, absorption appears at 1630 cm^{-1}, which is characteristic of the valency vibration of the —C=N— band.

The presence of absorption bands at 1600, 1580, and 1500 cm^{-1} indicates the appearance of an aromatic ring in the structure of the micromolecule[3] of the polymers investigated. The absorption band at 1460 cm^{-1} corresponds to the deformation vibration of the CH_2— group (Figs. 1(2) and 4). The curves (Fig. 4) show that the ratio of the optical density (D_1/D_2) of CH_2— groups at 1460 cm^{-1} up to 300°C hardly changes. These data indicate that the isocyanuric polymers are stable up to 300°C. By heating to a higher temperature the CH_2— groups considerably decrease, and at 500°C they disappear (Figs. 1 and 2). At 1390 and 1320 cm^{-1} the absorption corresponds to the vibration of C–N bonds.[18] This vibration remains unchanged up to 600°C. The absorption bands at 1260 and 1240 cm^{-1} correspond to the valency vibrations of C—O in the ester groups. The frequency of absorption at 1150–1060 cm^{-1} results from the valency vibration of C—O in —CH_2—O—CH_2— and the ester groups.[3] The shapes of the curves (Figs. 1(2) and 5) show that at a higher temperature of the polymers, the intensity of the bands corresponding to ester and ether groups decreases. It can be seen that the absorption bands corresponding to the ether groups decrease at a higher rate than those of the ester and other groups in temper-
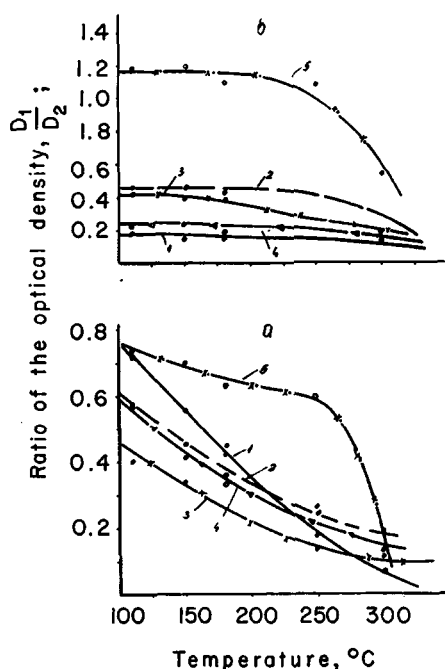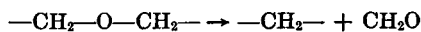
Fig. 5. Change in the ratio of optical densities with temperature (1)ALICPE-M; (2) ALICPE-MPh; (3) ALICPE-MA; (4) ALICPE-MS; (5) PPE-MPh; (a) D_1 (1120 cm^{-1})/D_2(765 cm^{-1}). (b) D_1 (1260 cm^{-1})/D_2(765 cm^{-1}).

ing the polymers. The fact that the degradation of the polymers begins with the methylene ether groups according to the scheme

$$—CH_2—O—CH_2— \rightarrow —CH_2— + CH_2O$$

is in line with published data.[17,19]

The absorption band at 990 cm^{-1} is in fact a combination of two bands, the one due to the plane deformation vibrations of the vinyl group —CH$_2$=CH—, and the other is characteristic of the out-of-plane deformation vibrations of —CH=CH—.[2,3,13] Taking into consideration the data published[3] and on the basis of the spectra of model mixtures produced by us, it should be assumed that the frequency at 935 cm^{-1} is also a combination of two bands, one corresponding to the out-of-plane deformation vibration of CH$_2$=CH—, and the other characterizing the out-of-plane deformation vibration of the OH group in carboxylic acids.[3] It is easy to notice that as a result of the hardening at the chosen temperature regime, these bands essentially decrease (Figs. 1(2) and 6). The double bonds practically react fully only after tempering the polymers at a higher temperature (Fig. 6). The curves (Fig. 6a and b) show that the polymerization ability of the double bonds depends measurably on the polymer's composition. The data show that by modification of the isocyanuric oligoester maleinates with phthalic, adipic, and sebacic acids, an increase of the speed of polymeriza-
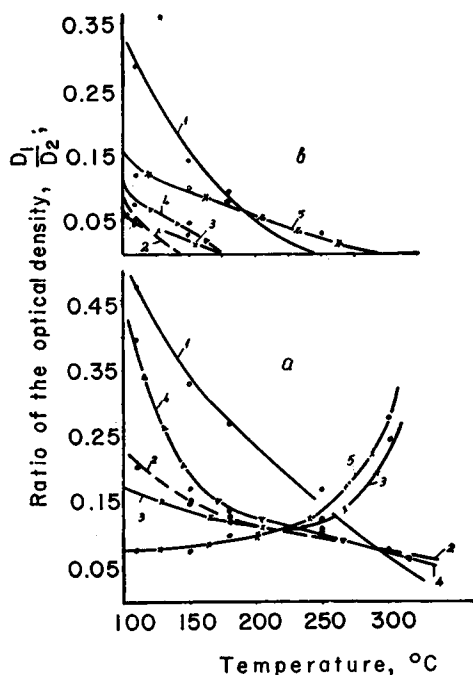
Fig. 6. Change in the ratio of the optical densities with temperature (1) ALICPE-M; (2) ALICPE-MHh; (3) ALICPE-MA; (4) ALICPE-MS; (5) PPE-MPh; (a) D_1 (935cm^{-1})/D_2(765 cm^{-1}). (b) D_1 (990 cm^{-4})/D_2(765 cm^{-1}).

tion is observed, followed by isomerization of the maleic double bonds to fumaric and by copolymerization at a higher rate.

The data show (Figs. 1(2) and 6b) that a built-in isocyanuric ring also accelerates the isomerization of maleinic double bonds to fumaric. As a result, absorption at 990 cm^{-1} precipitously decreases and disappears for ALICPE-MPh at 150°C, for ALICPE-MA and ALICPE-MS at 180°C, and for ALICPE-M at 250°C, whereas for PPE-MPh it disappears at 300°C. The ratio of the optical densities at 935 cm^{-1} of polymers containing an iso-cyanuric ring similarly shows a continuous decrease for ALICPE-M, ALICPE-MPh and ALICPE-MS; whereas for ALICPE-MA it reaches a minimum at 225°C after which it shows a tendency to rise. The curve of the optical density of PPE-MPh also shows an uninterrupted rise, and at 250°C it achieves a maximum. This can be explained by the fact that the absorption band at 935 cm^{-1} is a combination of out-of-plane deformation vibrations of CH_2=CH— and OH groups of carboxylic acids, and as a result of the polymerization of CH_2=CH— the curve shows a considerable de-crease (Fig. 6a) for ALICPE-M, ALICPE-MPh, ALICPE-MA, and ALICPE-MS. At a temperature above 250°C in ALICPE-MA, a process of oxidation and degradation of the polymer begins to take place at a measur-able rate, until monomers and oligomers containing a final carboxylic group are formed. The absorption of the OH group begins to increase (Fig. 6a)

as a result. Because of this, PPE-MPh contains no free $CH_2=CH-$
groups at 150°C, there is room only for the secondary processes, i.e., oxidation and destruction of the hardened polymer. The curve shows that this process hardly takes place initially up to 180°C; above 180°C it does take place at a moderate rate, and above 250°C it is extremely accelerated.

The fact that by degradation of polyester polymers carboxylic acids are separated corroborates published data.[19-21] The curves (Figs. 1 and 2) show that by tempering the polymers at 400°C, the absorption band at 935 cm^{-1} precipitously decreases and disappears at 500°C. At 765 cm^{-1}, the absorption band corresponds to that of the isocyanuric ring vibration,[13,22]
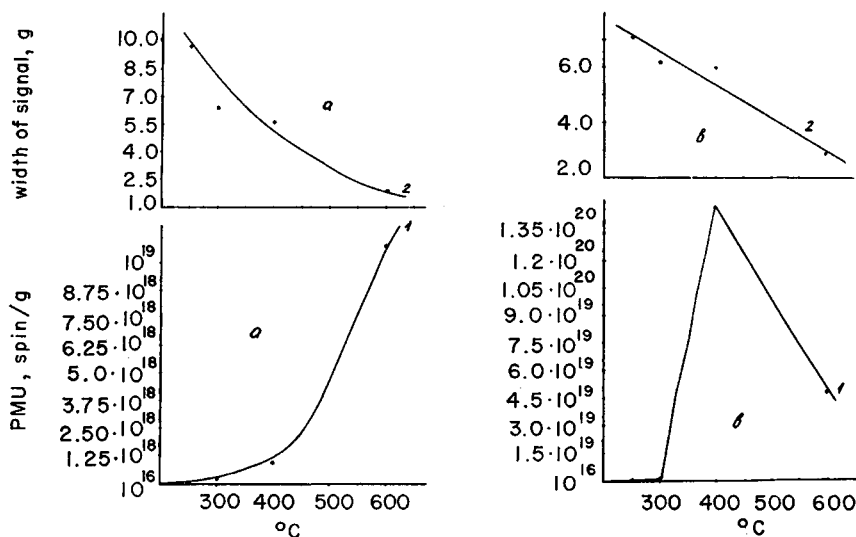

Fig. 7. Dependence of PMU concentration (1) and width of ESR signal (2) on temperature: (a) ALICPE-MPh; (b) PPE-MPh.

whereas at 700 cm^{-1}, the frequency absorption corresponds to the out-of-plane deformation vibrations of CH— in the aromatic ring.[3] The IR spectra (Figs. 1 and 2) show that these absorption bands decrease precipitously at 400°C and disappear at 500°C.

Typical ESR spectra of ALICPE-MPh and PPE-MPh are shown in Figure 7. They represent symmetrical singlets with a g-factor 2,0023 near the free electron. The ESR spectra prove that the products which have undergone thermal treatment contain radicals of prolonged life. The shapes of the curves in Figure 7a show that by increasing the temperature, the breadth of the signal decreases whereas the number of the PMU (paramagnetic units) increases. This is characteristic of all isocyanuric polymers, whereas in PPE-MPh (Fig. 7b) the greatest number of PMU is observed at 400°C.

On the basis of the investigation carried out, we assume that during hardening and thermal degradation of polymers, radicals play an essential part.

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