Analytical and Physical Investigation of Alkyd Resin in the Course of its Preparation. II. Study of Condensation Reaction and Molecular Weight Distribution of Alkyd

ALOIS KAŠTÁNEK, ŠTĚPÁN PODZIMEK, and KAREL HÁJEK,
*Research Institute for Synthetic Resins and Lacquers,
Pardubice, Czechoslovakia*

Synopsis

During preparation of alkyd resin by reaction between isocaprylic acid, phthalic anhydride, glycerol, and pentaerythritol the samples were successively taken away from the batch at different stages of the process and evaluated by analytical and physical ways. Acid numbers, hydroxyl numbers, and saponification numbers were determined by analyses of the samples and number-average molecular weights of alkyds were determined from vapor pressure osmotic measurements of their solutions. The extent of intramolecular esterification reactions (4–5 %) was determined from these values. Molecular weight polydispersities in alkyd samples prepared at higher degrees of conversion were estimated by means of GPC measurements, and weight-average molecular weight of the final alkyd resin was calculated by using theoretical relationships derived for nonlinear condensation polymers.

INTRODUCTION

Alkyd resins are prepared by esterification between carboxylic acids and polyalcohols[1-3]. Most frequently used polyalcohols are glycerol (functionality $f = 3$) and pentaerythritol ($f = 4$). Phthalic anhydride ($f = 2$) is often used as a bifunctional carboxylic acid. Monocarboxylic acids used for preparation of alkyd resins (usually unsaturated fatty acids of drying oils) terminate polyalcohols, depressing their functionalities. With respect to the content of reactants used for alkyd synthesis, nonlinear molecules with various degrees of branching are formed when a certain degree of conversion is reached and alkyd resin is characterized by certain molecular weight distribution. Quantitative theoretical treatment of molecular weight distribution in nonlinear polycondensates was carried out by Flory[4,5] and Stockmayer.[6] Later, Gordon[7] derived molecular weight distributions in nonlinear polymers. Jonasson[8] applied Flory's postulates to alkyds; other authors[9-12] went into problems of gelation during nonlinear polycondensation.

Degrees of conversion normally observed when gelation is reached differ from those determined for gel point by theory. Reasons of this discrepancy can be of various kinds. Sometimes, besides main esterification reactions between functional groups, the undesirable side reactions can also occur, for example, dehydration (etherification) of polyalcohols, decarboxylation of acids,[13,14] polymerization of chains of unsaturated fatty acids; at other

times, reactivities of functional groups are not equal. The most frequent reason of disagreement of theory with experiment is the occurrence of intramolecular esterification reactions. Occurrence of these reactions that accompany polyesterification reactions is stated by Jacobson and Stockmayer,[15] Stockmayer and Weil,[16] Gordon et al.,[17] and Berry.[18] Kienle et al.[19] mention that intramolecular reactions occur when glycerol reacts with dicarboxylic acids. Lum and Carlston[20] state that there is a great extent of formation of cyclic molecules if phthalic anhydride is used for alkyd synthesis.

Using the GPC for determination of molecular weight distributions in alkyd resins was described by Lesnini,[21] Bartosiewicz,[22] de la Court et al.,[23] Rybicka et al.,[24] Neises,[25] and Christensen and Fink-Jensen.[26] As elution volume–molecular weight calibrations are unknown for alkyd resins, apparent average molecular weights and apparent dispersion factors (given as a ratio of apparent weight-average molecular weight to apparent number-average molecular weight) are presented in the literature.

Our alkyd resin was prepared from phthalic anhydride, isocaprylic acid, glycerol, and pentaerythritol under conditions described in Ref. 27. The goal of this paper is to discover the eventual occurrence of side reactions (other reactions than esterification) and to determine the extent of intramolecular esterification reactions. We shall try to estimate polydispersity of molecular weights in final alkyd resin by using theoretical relationships for calculation of weight-average molecular weight and determine dispersion factors of alkyd samples by treatment of values obtained by GPC measurements of their solutions.

EXPERIMENTAL

Preparation of the Alkyd

Preparation of our alkyd resin is described in Ref. 27.

Analysis of Alkyd Resin

Determinations of acid number, hydroxyl number, and saponification number are described in Ref. 27, where, as well, their values for samples taken away at different stages of process are given.

Molecular Weight Determination

To determine the number-average molecular weights $\overline{M}_n$, a commercial apparatus (a Hewlett-Packard Model 302B VPO) based on the Hill-Blades vapor tension apparatus[28] was used. The measurements were carried out in acetone at 36°C. Four solutions of varying concentrations (0.01–0.1 mol/L) were measured. The apparatus was calibrated using pentaacetyl glucose.

GPC Measurements

For our measurements, a commercial liquid chromatograph (a Spectra-Physics Model 8100) consisting of four columns (a column is 25 cm long and its inner diameter is 7.7 mm) packed by Microgel of different perme-

ability (100, 500, 10^3, and 10^4 Å) was used. Tetrahydrofuran was used as a solvent, temperature of GPC measurements was 40°C, the flow rate was 1 mL/min, volumes of injected samples were 10^{-4} L. An RI detector (a Waters Model R 401) and a UV/VIS analyzer (a Spectra-Physics Model 8440) adjusted to the wavelength of 254 nm were used for identification of the eluted alkyd. Plots and evaluations of elution curves were carried out by means of the integrator (a Spectra-Physics Model 4200). The set of used columns was calibrated by polystyrene standards (Waters Assoc.).

RESULTS

Treatment of the Values Obtained by Alkyd Analyses and VPO Measurements

Number-average molecular weights $\overline{M}_n$, of reaction mixture, numbers n of moles of all homologues contained in 1 g of reaction mixture, numbers n_A of moles of unreacted carboxylic groups contained in 1 g of reaction mixture, and numbers n_B of moles of unreacted hydroxyl groups contained in 1 g of reaction mixture at different stages of the process (at j th stages of the process) are given in Table I. Values of n, n_A, and n_B were calculated by means of

$$n = \overline{M}_n^{-1} \tag{1}$$

$$n_A = 1.7825 \times 10^{-5} n_a \tag{2}$$

$$n_B = 1.7825 \times 10^{-5} n_h \tag{3}$$

where n_a is the acid number and n_h is the hydroxyl number.[27]

Degree of conversion, p_A, of carboxylic groups (see Table I) is defined by

$$p_A = \frac{n_s - n_a}{n_s} \tag{4}$$

TABLE I
Results of Analyses and VPO Measurements of Alkyd Resins

j	p_A	$\overline{M}_n$	$n \times 10^3$	$n_A \times 10^3$	$n_B \times 10^3$
1	0.464	250	4.00	3.770	4.911
2	0.554	300	3.33	3.228	4.253
3	0.630	330	3.03	2.722	3.813
4	0.716	400	2.50	2.112	3.226
5	0.797	560	1.78	1.536	2.663
6	0.896	860	1.16	0.797	1.966
7	0.927	1050	0.95	0.565	1.691
8	0.932	1200	0.83	0.526	1.711
9	0.958	1400	0.71	0.323	1.520
10	0.962	1420	0.70	0.292	1.449

where n_s is the saponification number.[27]

Degree of conversion, p_B, of hydroxyl groups is defined by

$$p_B = \frac{n_s - n_a}{n_s - n_a + n_h} \tag{5}$$

Dependences n_a resp. $n_a n_{s,1} n_s^{-1} - p_A$ and n_h resp. $n_h n_{s,1} n_s^{-1} - p_A$ are given in Figure 1, dependences n_a resp. $n_a n_{s,1} n_s^{-1} - p_B$ and n_h resp. $n_h n_{s,1} n_s^{-1} - p_B$ are given in Figure 2. Both corrected dependences in each figure are linear and parallel one to another. Choice of $n_{s,1}$ for correction factors $n_{s,1} n_s^{-1}$ is arbitrary. If other correction factors ($n_{s,2} n_s^{-1}$, $n_{s,3} n_s^{-1}$ ...) were used, our corrected dependences would be linear and parallel again. Resulting from discussion of these dependences, the extent of side reactions (other reactions than esterification) may be considered to be negligible during alkyd synthesis.

The ratio of the total number n_{B0} of moles of all hydroxyl groups (reacted and unreacted) to total number n_{A0} of moles of all carboxylic groups (reacted and unreacted) for each sample withdrawn from the batch is given by

$$\frac{n_{B0}}{n_{A0}} = \frac{n_s - n_a + n_h}{n_s} \tag{6}$$

A mean ratio n_{B0}/n_{A0} is 1.15. Maximum deviation from this mean value is $\pm$ 0.004 for all samples withdrawn at different stages of the process. As the amounts of all reactants in the original reaction mixture are known as well as the losses of isocaprylic acid (mean loss is 49 g) and glycerol (mean loss is 13 g) from reaction mixture,[27] the mean ratio R_{A0} of the total number of moles of carboxylic groups (reacted and unreacted) belonging to phthalic acid to the total number of moles of carboxylic groups belonging
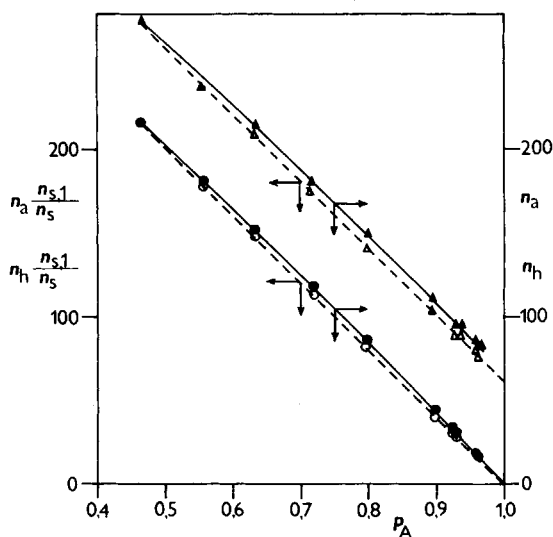

Fig. 1. Dependences: ($\bullet$)$n_a - p_A$; ($\blacktriangle$)$n_h - p_A$; ($\bigcirc$)$n_a n_{s,1} n_s^{-1} - p_A$; ($\triangle$)$n_h n_{s,1} n_s^{-1} - p_A$.
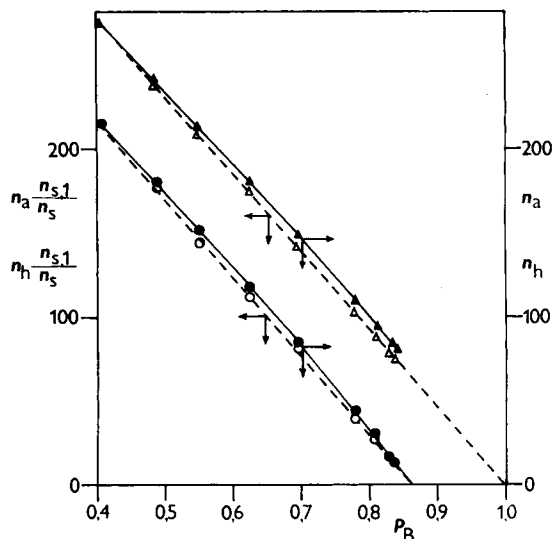
Fig. 2. Dependences: ($\bullet$)$n_a - p_B$; ($\blacktriangle$)$n_h - p_B$; ($\bigcirc$)$n_a n_{s,1} n_s^{-1} - p_B$; ($\triangle$)$n_h n_{s,1} n_s^{-1} - p_B$.

to isocaprylic acid ($R_{A0} = 1.67$), and mean ratio R_{B0} of the total number of moles of hydroxyl groups belonging to pentaerythritol to the total number of moles of hydroxyl groups belonging to glycerol ($R_{B0} = 2.15$) could be determined.

By means of determined acid numbers, hydroxyl numbers, and saponification numbers of reaction mixture[27] at stages of the process $j = 6$–10, the total number of moles of functional groups (reacted and unreacted) belonging to each component in 1 g of alkyd was calculated, so that the number of moles of each component is known as well. The total number n_0 of moles of all components contained in 1 g of reaction mixture is given in Table II.

As the samples withdrawn at later stages of the process than $j = 5$ contain only very small amounts of water,[27] the number-average molecular weights $\overline{M}_n$ of these samples represents directly the number-average molecular weights of alkyd resins. If we simply consider water as an nonvolatile substance, whose content in j th withdrawn sample is $w_{W,j}$, we can calculate the number-average molecular weight of alkyd resin contained in the j th sample. For example, $\overline{M}_n$ of the 6th sample, which contains the greatest amount of water (0.08 %) comparing the five last withdrawn samples, is 860, and calculated number-average molecular weight of alkyd resin con-

TABLE II
Formation of Cycles in Alkyd Resin

j	p_A	p_m	$p_{m,ap}$	$n_0 \times 10^3$	$\overline{x}_n$	$2n_r \times 10^3$	$2N_r \times 10^2$
6	0.896	0.833	0.792	7.716	6.64	0.676	4.9
7	0.927	0.864	0.820	7.733	8.12	0.717	5.0
8	0.932	0.865	0.834	7.758	9.31	0.519	3.6
9	0.958	0.889	0.848	7.762	10.87	0.680	4.6
10	0.962	0.895	0.850	7.749	11.00	0.745	5.0

tained in the 6th sample is 890. The difference between both molecular weights is relatively very small (ca. 3%). Thus calculations of polymerization degree of alkyd [eq. (7)] and quantity of intramolecular reactions [eq. (10)] are not essentially affected by using value of $\overline{M}_n$ of the sample.

The number-average polymerization degree $\bar{x}_n$ of alkyd resin (see Table II) can be determined by means of

$$\bar{x}_n = n_0\overline{M}_n \tag{7}$$

where n_0 is the total number of moles of all components contained in 1 g of the sample.

If esterification occurs not only between functional groups belonging to different molecules, eq. (8) applies[29]:

$$\bar{x}_n = \frac{1}{1 - 0.5p_{m,ap}f_m} \tag{8}$$

where f_m is the mean functionality expressed as a ratio of total number of moles of all functional groups (reacted and unreacted) to total number of moles of all components, $p_{m,ap}$ is the apparent degree of conversion. The apparent degree of conversion means the degree of conversion that corresponds to the real polymerization degree $\bar{x}_n$ and that would be reached if intermolecular reactions of functional groups only occurred. The real degree of conversion, p_m, which is higher than $p_{m,ap}$, is expressed as the ratio of number of moles of all reacted functional groups to the total number of moles of all functional groups (reacted and unreacted). By means of eq. (8) the values of $p_{m,ap}$ of the samples of reaction mixture at stages of the process $j = 6-10$ were calculated and are given together with the values of p_m in Table II.

The number $2n_r$ of moles of functional groups (in 1 g of the sample), which have reacted by esterification reactions between functional groups belonging to the same molecules (intramolecularly), is given

$$2n_r = (n_{A0} + n_{B0})(1 - p_{m,ap}) - n_A - n_B \tag{9}$$

where n_r is the number of moles of cycles in 1 g of the sample, $n_{A0} + n_{B0}$ is the total number of moles of all functional groups (reacted and unreacted) contained in 1 g of the sample, n_A (resp. n_B) is the number of moles of unreacted carboxylic groups (resp. unreacted hydroxyl groups) contained in 1 g of the sample.

Percent content $2N_r \times 10^2$ of the number of moles of functional groups that reacted intramolecularly (the number of moles of all reacted functional groups corresponds to 100%) is given by

$$2N_r \times 10^2 = \frac{2n_r \times 10^2}{n_{A0} + n_{B0} - n_A - n_B} \tag{10}$$

Values of $2n_r$ and $2N_r \times 10^2$ are given in Table II.

TABLE III
Values $\bar{x}_n^+$ and $\overline{M}_n^+$ of Alkyds Supposing Only Intermolecular Reactions

j	P_A	$\bar{x}_n$	$\bar{x}_n^+$	$\overline{M}_n$	$\overline{M}_n^+$
6	0.896	6.64	9.37	860	1210
7	0.927	8.12	13.03	1050	1680
8	0.932	9.13	13.52	1200	1740
9	0.958	10.87	20.76	1400	2670
10	0.962	11.00	23.37	1420	3020

Values $\bar{x}_n^+$ and $\overline{M}_n^+$ are given in Table III. Number-average polymerization degree $\bar{x}_n^+$ was calculated by means of

$$\bar{x}_n^+ = \frac{1}{1 - 0.5 p_m f_m} \qquad (11)$$

Dependence of $\overline{M}_n^+$ ($\overline{M}_n^+$ is a hypothetical number-average molecular weight that was calculated admitting only intermolecular reactions of all reacted functional groups) on the degree of conversion p_A and dependence of $\overline{M}_n$ of our alkyd on p_A are shown in Figure 3. As is evident from Figure 3, differences between $\overline{M}_n^+$ and $\overline{M}_n$ are small at lower degrees of conversion; however, they increase as conversion proceeds, and the difference is big enough at $p_A = 0.96$ ($\overline{M}_n^+ = 2800$, $\overline{M}_n = 1400$).

Evaluation of GPC Measurements

Elution curves of alkyds withdrawn at different stages of the process are shown in Figure 4. It is evident that the losses of portions of low molecular weights are continuous and molecular weight distributions shift to higher molecular weights as conversion proceeds. By treatments of values obtained from evaluations of elution curves using calibration valid for polystyrene, the average molecular weights, and dispersion factors for four last samples were determined. The results are given in Table IV.
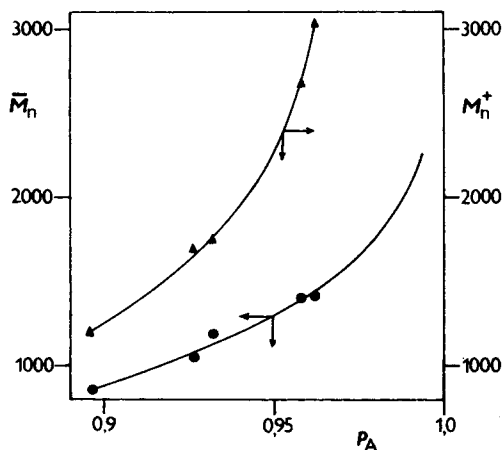

Fig. 3. Dependences: ($\bullet$)$\overline{M}_n - p_A$; ($\blacktriangle$)$\overline{M}_n^+ - p_A$.
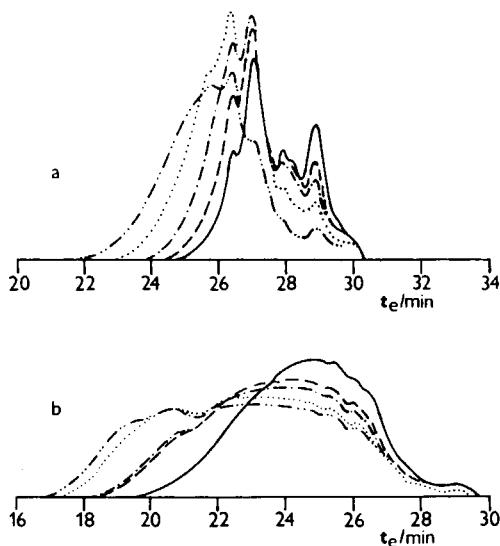
Fig. 4. Dependence of UV-analyzer signal at wave length 254 nm on elution time: (a) samples 1 (———), 2 (- - -), 3 (-·-), 4 (· · ·), 5 (- · · -); (b) samples 6 (———), 7 (- - -), 8 (-· ·-), 9 (· · ·), 10 (- · · -).

Use of Theoretical Relationships for Determination of Molecular Weight Polydispersity in Alkyd Resin

We used eq. (12) for calculation of weight-average molecular weight $\overline{M}_w$ of alkyd sample withdrawn at stage of the process $j=10$ ($p_A = 0.962$). Equation (12) was derived[6] according to the theory of molecular weight distribution in polymers formed by polycondensation of monomers of functionalities $f \geq 2$ presuming equal reactivities of functional groups and neglecting intramolecular reactions:

$$\overline{M}_w = \frac{p_{B12} \dfrac{M(A)_1^2 A_1}{f_1 A_1} + p_{A1} \dfrac{\overline{M}(B)_1^2 B_1 + \overline{M}(B)_2^2 B_2}{\bar{g}_1 B_1 + \bar{g}_2 B_2} + p_{A1} p_{B12} F}{p_{B12} \dfrac{M(A)_1 A_1}{f_1 A_1} + p_{A1} \dfrac{\overline{M}(B)_1 B_1 + \overline{M}(B)_2 B_2}{\bar{g}_1 B_1 + \bar{g}_2 B_2}} \tag{12}$$

where

$$F = \frac{p_{A1}(f_e - 1)M_b^2 + p_{B12}(g_e - 1)M_a^2 + 2M_a M_b}{1 - p_{A1} p_{B12}(f_e - 1)(g_e - 1)} \tag{13}$$

TABLE IV
Evaluation of GPC Measurements

j	$\overline{M}_n$ (GPC)	$\overline{M}_w$ (GPC)	$\overline{M}_w$ (GPC)/$\overline{M}_n$ (GPC)
7	1980	3520	1.8
8	2040	3780	1.9
9	2490	6330	2.5
10	2620	7900	3.0

$$f_e = f_1^2 A_1 (f_1 A_1)^{-1} = f_1 \tag{14}$$

$$g_e = (\bar{g}_1^2 B_1 + \bar{g}_2^2 B_2)(\bar{g}_1 B_1 + \bar{g}_2 B_2)^{-1} \tag{15}$$

$$M_a = M_1 f_1 A_1 (f_1 A_1)^{-1} = M_1 \tag{16}$$

$$M_b = [\overline{M}(B)_1 \bar{g}_1 B_1 + \overline{M}(B)_2 \bar{g}_2 B_2](\bar{g}_1 B_1 + \bar{g}_2 B_2)^{-1} \tag{17}$$

The assumption that carboxylic groups of all molecules of isocaprylic acid have reacted with hydroxyl groups (thus depressing functionalities of glycerol and pentaerythritol to the maximum extent) is practically realized at higher degrees of conversion. We can regard alkyd resin as a polymer compound that was formed by esterification reactions between phthalic acid and the derivatives of glycerol and pentaerythritol with isocaprylic acid. Derivatives of glycerol have mean functionality $\bar{g}_1$ ($\bar{g}_1 = 2.024$) and mean molecular weight $\overline{M}(B)_1$ [$\overline{M}(B)_1 = 197.2$], derivatives of pentaerythritol have mean functionality $\bar{g}_2$($\bar{g}_2 = 2.697$), and mean molecular weight $\overline{M}(B)_2$ [$\overline{M}(B)_2 = 276.19$]. In fact, polydispersities of functionalities (the real functionalities are integers) and molecular weights of derivatives exist. Neglecting these facts results in partial depressing calculated value of $\overline{M}_w$.

Further symbols in eqs. (12) and (13) designate the following: A_1 is the number of moles of phthalic acid in 1 g of the sample ($A_1 = 2.411 \times 10^{-3}$), B_1 (resp. B_2) is the number of moles of all derivatives of glycerol with isocaprylic acid (resp. pentaerythritol) with isocaprylic acid in 1 g of the sample ($B_1 = 9.38 \times 10^{-4}$, $B_2 = 15.13 \times 10^{-4}$), $M(A)_1$ is the molecular weight of phthalic acid lowered by 18 [$M(A)_1 = 148.1$], f_1 is the functionality of phthalic acid ($f_1 = 2$), g_e is the average functionality of derivatives possessing hydroxyl groups ($g_e = 2.4835$) calculated by means of eq. (15), M_b is the average molecular weight of derivatives possessing hydroxyl groups ($M_b = 251.13$) calculated by means of eq. (17), p_{A1} is the degree of conversion of carboxylic groups belonging to phthalic acid ($p_{A1} = 0.862$), p_{B12} is the degree of conversion of hydroxyl groups of derivatives of glycerol and pentaerythritol with isocaprylic acid ($p_{B12} = 0.695$). When p_{A1} (resp. p_{B12}) are calculated, it is necessary to add the number n_r of moles of cycles to number n_A (resp. n_B) of moles of unreacted functional groups.

The calculated value of $\overline{M}_w$ is 6150.

DISCUSSION

Using the correction factor $n_{s,1} n_s^{-1}$ (it is present in the terms $n_a n_{s,1} n_s^{-1}$ and $n_h n_{s,1} n_s^{-1}$) is desirable with regard to the loss of water formed by esterification from reaction mixture. The courses of dependences $n_a n_{s,1} n_s^{-1} - p_A$ and $n_h n_{s,1} n_s^{-1} - p_A$ shown in Figure 1 are linear and parallel to each other. This is always typical when no side reactions occur and esterification is the only reaction of functional groups.

In case no etherification but decarboxylation (resp. sublimation of phthalic anhydride formed by deesterification from reaction mixture) occurred to a certain extent at $p_A > 0.464$, the courses of the two corrected above-mentioned dependences would not be parallel to each other; their difference would be bigger compared with the one of our dependences at $p_A = 0.962$.

In case no decarboxylation (resp. sublimation of phthalic anhydride from reaction mixture) but etherification occurred to a certain extent at $p_A > 0.464$, the courses of both corrected dependences would not be parallel to each other again; their difference would be smaller compared with the one of our dependences at $p_A = 0.962$. In case decarboxylation (event. sublimation of phthalic anhydride from reaction mixture) and etherification occurred to a certain extent at $p_A > 0.464$ and the extents of both side reactions were equal, the differences of both corrected dependences would be equal at different p_A. In fact, however, it is not probable that the extents of both side reactions would be equal.

So, the fact that the courses of both corrected dependences shown in Figure 1 are linear and parallel one to another indicates that the extent of side reactions is very probably negligible during synthesis of our alkyd. The same may be concluded if we consider the dependences shown in Figure 2. As well, our conclusions are supported by good agreement of measured amounts of water distilled off during alkyd synthesis with calculated amounts of water losses from the batch admitting esterification reaction only.[27]

The main reason for greater conversion of functional groups than corresponds to the number of formed polymer molecules (by intermolecular esterification reactions) is obviously the occurrence of intramolecular esterification reactions of functional groups belonging to the same molecules. In case of nonlinear polycondensates, unlike linear ones, the formations of cycles of lower polymerization degrees (they are probable) can take place at later stages of process too, so that the extent of intramolecular reactions does not become negligible when no diluent of reaction mixture is used. The occurrence of two adjacent carboxylic groups in molecules of phthalic acid favors the extent of intramolecular reactions; as well, the cycles formed by reaction of one molecule of phthalic anhydride with one molecule of glycerol (resp. pentaerythritol)[20] arise very easily.

The critical degree of conversion p_{Ac}^+ ($p_{Ac}^+ = 0.947$) was calculated by means of

$$(p_{A1}^+ p_{B12}^+)_c = \frac{1}{(f_e - 1)(g_e - 1)} \tag{18}$$

Degree of conversion, p_A, of the sample at stage of the process $j = 10$ is 0.962. It means, if intramolecular reactions were absent, reaction mixture would have gelled before reaching this degree of conversion. The critical number-average molecular weight $\overline{M}_{nc}^+ = 2130$ corresponds to $p_{Ac}^+ = 0.947$. In the course of synthesis of our alkyd, it would be necessary to reach somewhat higher molecular weight than $\overline{M}_{nc}^+$ (with regard to unequal reactivities of hydroxyl groups and influence of intramolecular reactions on depressing functionalities of reactants) in order that the gelation could be observed.

The real value of $\overline{M}_w$ of our alkyd ($\overline{M}_n = 1420$) ought to be something lower than 6150 [6150 is a value of $\overline{M}_w$ calculated by means of eq. (12) when unequal reactivities of hydroxyl groups and influence of intramolecular reactions on depressing functionalities of reactants are neglected]. As well,

a real value of dispersion factor $\overline{M}_w/\overline{M}_n$ ought to be something lower than 4.3 [4.3 is a value of $\overline{M}_w/\overline{M}_n$ calculated by using $\overline{M}_w$ determined by means of eq. (12)]. The value of the dispersion factor $\overline{M}_w$ (GPC)/$\overline{M}_n$ (GPC) determined from GPC measurements is 3.0. This value will not be quite correct either [the values of $\overline{M}_w$ (GPC) and $\overline{M}_n$ (GPC) determined from GPC measurements differ surely from real values of $\overline{M}_w$ and $\overline{M}_n$; however, the values of $\overline{M}_w$ (GPC)/$\overline{M}_n$ (GPC) do not differ from real values of $\overline{M}_w/\overline{M}_n$ so significantly].

Composition of alkyd resins is described by two parameters[26] L, the ratio of monocarboxylic acid equivalents to total acid equivalents, and H (hydroxyl excess), the ratio of polyol equivalents to acid equivalents. Values of these parameters of our alkyd are $L = 0.374$ and $H = 1.150$. Comparison of the dispersion factor determined for our final alkyd at $p_A = 0.962$ [$\overline{M}_w$ (GPC)/$\overline{M}_n$ (GPC) = 3.0] with the dispersion factor of alkyd[26] prepared from tall oil fatty acids, phthalic anhydride, and pentaerythritol, which has similar parameters p_A, L, and H to our alkyd, shows that the values of both dispersion factors determined from GPC measurements coincide fairly well.

CONCLUSION

It was found out that the coefficient of polydispersity of molecular weights determined experimentally (from GPC measurements) for alkyd resin prepared from isocaprylic acid, phthalic anhydride, glycerol, and pentaerythritol (composition of the resin is characterized by parameters $L = 0.374$ and $H = 1.150$) at a final degree of conversion, $p_A = 0.962$ is somewhat lower than the coefficient of polydispersity calculated by means of relationships derived from the theory of molecular weight distribution in nonlinear polycondensates [$\overline{M}_w$ (GPC)/$\overline{M}_n$ (GPC) = 3.0, $\overline{M}_w/\overline{M}_n$ = 4.3). The real value of coefficient of molecular weight polydispersity should be somewhat lower than 4.3 with regard to unequal reactivities of functional groups and the influence of intramolecular reactions on depressing the functionalities of reactants that were not taken in account calculating $\overline{M}_w$ by means of eq. (12).

Higher conversion of functional groups than that corresponding to the number of polymer molecules formed (by intermolecular esterification reactions) is most probably caused by intramolecular reactions of functional groups. Considering intramolecular reactions as the only reason for the above-mentioned fact, the extent of intramolecular reactions was determined to be 4–5% at $p_A = 0.96$.

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