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Molecular masses and characteristics of polyethileneglycolmaleate, polypropyleneglycolmaleate, polyethileneglycolphthalate, polypropyleneglycolphthalate

The molecular masses and characteristics of such unsaturated polyester resins as polyethyleneglycolmaleate, polypropyleneglycolmaleate, polyethyleneglycolphthalate and polypropyleneglycolphthalate were studied. It was determined the weight average molecular weight and number average molecular weight of unsaturated polyester resins, and it was carried out the comparative analysis of the obtained data.

Key words: unsaturated polyester resin, number-average molecular weight, weight-average molecular weight.

Introduction

Molecular mass and polydispersity degree belong to the main characteristics of high-molecular compound, because of physical and chemical properties of polymers directly depend on the sizes of the molecules arranged by certain type [1]. Various methods are used for the experimental determination of the molecular weight of the polymers; some of them determine number-average meanings (osmometry, the method of terminal groups) and others — weight-average (light-scattering method) [2]. Therefore, the molecular weight meaning of the polymer determined by means of one or other method is the average value.

It was interesting to study average molecular mass of unsaturated polyester resins. Over the past few decades, unsaturated polyester resins are widely recognized as highly reliable products with chemical and temperature resistance combined and excellent mechanical properties [3]. The simplicity of the synthesis allows to suggest that scope of use of such polymer system will be expanded rapidly.

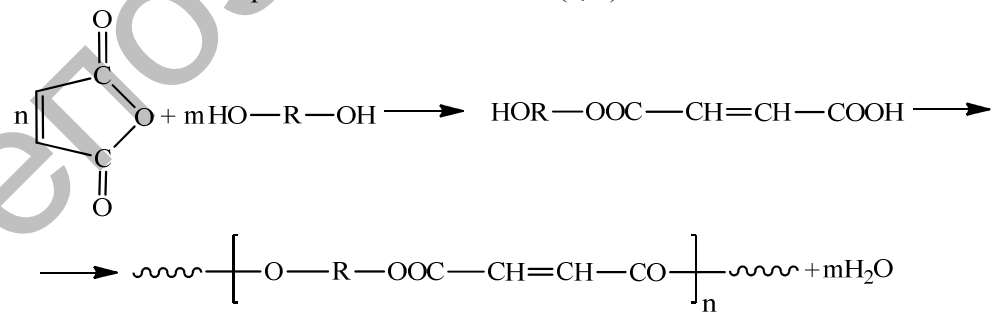
The following unsaturated polyester resins as (polyethyleneglicol) maleate, phthalate, (polypropeleneglycol) maleate, phthalate were chosen as the objects of the investigation.

Experimental part

Unsaturated polyester resins were produced by the polycondensation of glycols (ethylene glycol, propyleneglicol) with anhydrides of unsaturated dicarboxylic acids (toxilic anhydride, phthalic anhydride) at the temperature of 413–433 K [4]. The monitoring of the reaction course was performed by acid number determining.

The course of reactions is represented on the schemes (a, b):

a)



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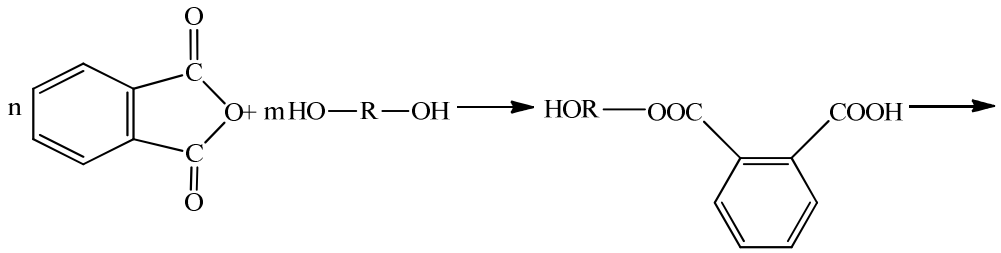

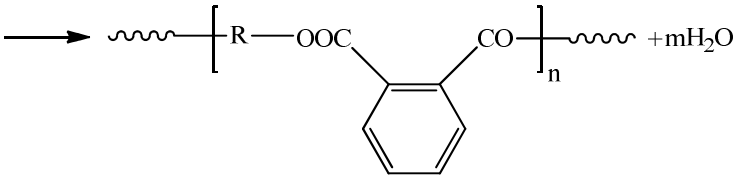

Indexes of acid and hydroxyl numbers of the samples were determined by the titrimetry [5]. Acid number ($A.N.$) was estimated according to the formula:

$$A.N. = \frac{(V_1 - V_2) \times f \times 0{,}00561 \times 1000}{a}, \quad (1)$$

where 0,00561 — titer of 0,1 solution of KOH, g/ml.

Hydroxyl number ($H.N.$) was calculated according to the formula:

$$H.N. = \frac{(V_1 - V_2) \times f \times 0{,}028 \times 1000}{a}, \quad (2)$$

where 0,028 — titer of 0,5 solution of KOH, g/ml.

Yield mass calculation for the certain acid number $A_{A.N.}$ was determined according to the formula:

$$A_{A.N.} = \frac{A_0}{1 - \frac{A.N. \times M_{H_2O}}{M_{KOH} \times 1000}}, \quad (3)$$

where A_0 — yield mass for $A.N. = 0$

The number of unreacted carboxyl groups ν_{COOH} was estimated according to the formula:

$$\nu_{COOH} = \frac{A.N. \times A_{A.N.}}{M_{KOH} \times 1000}.$$

Number-average molecular weight was calculated according to the formula:

$$\bar{M}_n = \frac{A_{A.N.}}{n_2 \times (K_M - 1)},$$

where K_M — constant of polycondensation, that was determined according to the formula:

$$K_M = \frac{n_1 + \nu_{COOH}}{n_2}.$$

Number-average molecular mass of polymers was determined by the light-scattering method [6, 7] in the nephelometer HACH 2100AN. Measurement was carried out according to the laboratory standards [8]. Molecular mass was determined according to the formula:

$$\frac{HC}{R_{\theta i}} = \frac{1}{M_w} + \frac{2BC}{RT},$$

where H — optical constant, that is equal to

$$H = \frac{32\pi^3}{3} \frac{n_0^2}{N_A \lambda_0^4} \left(\frac{dn}{dc}\right)^2,$$

where C — is the polymer concentration in the solution, g/100 ml; $R_{\theta i}$ — is hyper intensity of light scattered at an angle 90º; λ_0 is the wave length of applied light; N_A is Avogadro number; dn / dc — refractive index increment, that was measured in refractometer IRF-23.

Determinations of the main objects of the study are represented in this work with the list of numerical characteristics of results reproducibility.

Degree of polydispersity D_M was estimated according to the formula:

$$D_M = \frac{\bar{M}_w}{\bar{M}_n},$$

where $\bar{M}_w$ — average molecular mass; $\bar{M}_n$ — number-average molecular mass.

Results and discussion

The most important peculiarities of unsaturated polyester resins are their molecular mass meanings and molecular mass ratio, these properties determine practical usefulness of polymers [1].

The average meanings of molecular weight and molecular mass of unsaturated polyester resins were determined in this study; and it was carried out the comparative analysis of the data [2]. Some characteristics of unsaturated polyester resins are represented in Table 1.

Table 1

Indexes of acid and hydroxyl numbers of unsaturated polyester resins

UPR	Index								
	A.N., mg KOH/g	ν_{COOH}, mole	*H.N.*, mg KOH/g	ν_{OH}, mole	A_0, g	$A_{A.N.}$, g	K_M	Water, g	$\bar{M}_n$, g/mole
p-EGPH	15,07	0,08	29,07	0,23	371,37	373,18	1,11	23,37	2001,58
p-EGM	21,39	0,26	26,12	0,57	659,43	663,98	1,18	33,30	1881,25
p-PGPH	14,51	0,08	28,51	0,24	399,39	401,25	1,11	23,47	2112,57
p-PGM	20,19	0,25	26,19	0,58	726,07	730,81	1,17	30,83	1996,40

As it follows from the obtained data, the indexes of acid numbers of derived products reveal substantial decreasing of carboxyl groups at the reaction process (acid numbers are within limits of 15,05–20,20 mg KOH/g). Yield masses of unsaturated polyester resins for the certain acid number $(A_{A.N.})$ is larger than yield mass of unsaturated polyester resins when $A.N. = 0$ (A_0) to the amount of released water, consequently, reactivity ratio are $K_M > 1$. The number of unreacted carboxyl groups decreases, and the number of excessive carboxyl groups increases. *A.N.* — acid numbers of the samples containing phthalic anhydride are slightly below, apparently, it is caused by the maximal interaction reaction rate of the phthalic acid anhydride with OH-group of alcohol, and this rate is preferable.

Number-average molecular weight determined according to by acid number (Table 1) is slightly higher for propylene polymers than for residues of the ethylene glycol; that is definitely due to a high-mobility of the hydroxyl groups.

In a continuation of the study, the weight-average molecular weight of polymers was determined by the using of light-scattering method. This method technically isn't difficult and it doesn't require preliminary plotting of calibration curve with using of polymer fractions with known molecular mass, therefore, that is absolute method [8]. Turbidness of polymers solutions was determined by the turbidity method at λ=546 nm. Obtained data were processed by mathematical statistics method, according to the equation (7) and (8); and then $\frac{HC}{R_{\theta i}} - f(C)$ plots were depicted (Fig. 1, 2).

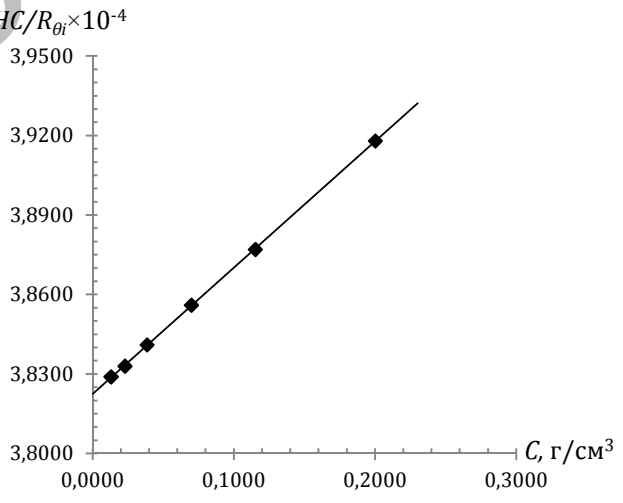

Figure 1. Dependence $HC / R_{\theta i}$ on C for dilute solutions of p-PGPH in chloroform

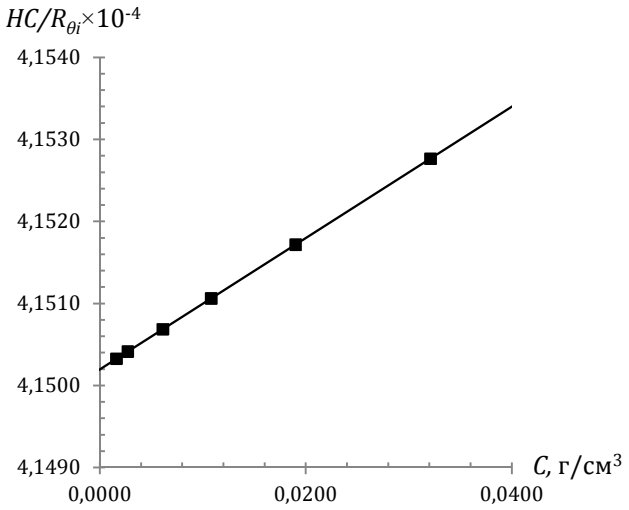

Figure 2. Dependence of $HC / R_{\theta i}$ from C for dilute solutions of p-PGM in chloroform

Curves at the Figures 1, 2 are typical for dilute solutions of polymer. Data was determined by the extrapolation of $\frac{HC}{R_{\theta i}}$ correlation from C to zero-concentration $C = 0$ of the polymer, according to the formula:

$$\left(\frac{HC}{R_{\theta i}}\right)_{c\to 0} = \frac{1}{\bar{M}}.$$

Therefore, intercept on the Y-axis cut by envelope curve gives us the meanings that were estimated according to a formula (10), and this formula helps to determine mass-averaged molecular masses of polymers represented in the Table 2.

All experimentally obtained values were checked by metrological testing.

Table 2

Molecular characteristics of unsaturated polyester resins

Object	$H\times10^{-8}$	$\left(\frac{HC}{R_{\theta i}}\right)_{c\to 0} = \frac{1}{\bar{M}}\times10^{-4}$	$\bar{M}_w$
p-EGPH	13,6380	3,9300	2544,53
p-EGM	6,7879	4,2400	2358,49
p-PGPH	5,0214	3,8250	2614,38
p-PGM	7,8168	4,1502	2408,48

The molecular weights and peculiarities of unsaturated polyester resins (UPR) determined by light scattering method and by terminal group analysis are represented at the Table 3.

Table 3

Molecular masses of UPR determined by light scattering and by terminal group analysis

Object	$\bar{M}_n$, g/mole	$\bar{M}_w$, g/mole	D_M	Yield, %
p-EGPH	2001,58	2544,53	1,27	98,9
p-EGM	1881,25	2358,49	1,25	98,6
p-PGPH	2112,57	2614,38	1,24	98,2
p-PGM	1996,40	2408,48	1,21	98,1

Comparison of the results represented in Table 3 reveal that $\bar{M}_w > \bar{M}_n$, and this correlates well with the literature data. High D_M value indicates a high index of polymers polydispersity, and it will be reasonable to expect on polycondensation reactions.

Conclusions

Therefore, it was revealed that polymers with minor molecular masses and high degree of polydispersity were obtained in the polycondensation reaction of dicarboxylic acid anhydrites with glycols.

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Полиэтиленгликольмалеинат, полипропиленгликольмалеинат, полиэтиленгликольфталат және полипропиленгликольфталаттың сипаттамасы және молекулалық массалары

Полиэтиленгликольмалеинат, полипропиленгликольмалеинат, полиэтиленгликольфталат және полипропиленгликольфталат қанықпаған полиэфир шайырларының молекулалық сипаттамалары және массалары зерттелді. Қанықпаған полиэфир шайырларының массасы және салмағы бойынша молекулалық орташа мәні анықталып, алынған мәліметтерге салыстырмалы талдау жүргізілді.

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Молекулярные массы и характеристики полиэтиленгликольмалеината, полипропиленгликольмалеината, полиэтиленгликольфталата и полипропиленгликольфталата

Исследованы молекулярные массы и характеристики следующих ненасыщенных полиэфирных смол: полиэтиленгликольмалеината, полипропиленгликольмалеината, полиэтиленгликольфталата, полипропиленгликольфталата. Определены средние значения молекулярных по весу и массе ненасыщенных полиэфирных смол, и проведен сравнительный анализ полученных данных.

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