FEATURES OF HYDRODYNAMIC AND MOLECULAR WEIGHT CHARACTERISTICS OF HOMO AND COPOLYMERS 2, 4, 5 - TRICHLOROPHENYLACRYLATE

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ABSTRACT:

The article studies the hydrodynamic and conformational properties of polytrichlorophenylacrylate, copolymers of N-vinylpyrrolidone with trichlorophenylacrylate and trichlorophenylmethacrylate. Based on sedimentation, diffusiometric and viscometric studies, the parameters of the Mark-Kun-Hauwink equations are determined

KEYWORDS: trichlorophenyl acrylate, diffuometer, refractive index increments, hydrodynamic invariant, Kuhn segment, sedimentogram, vinylpyrrolidone.

INTRODUCTION:

Reactive polymers are an interesting class of polymer carriers that can be used in various fields of the synthesis of specific substances for medicine, agriculture, catalysis, etc. [1-6]. Such polymers include copolymers of vinylpyrrolidone (VP) with 2,4,5-trichlorophenyl (meth) acrylate (TCFM).Samples of p-trichlorophenyl acrylate were obtained by radical polymerization of trichlorophenyl acrylate at 65 ° C in dioxane at a varying concentration of dinitrile azo-bisisobutyrate initiator. The conversion does not exceed 12%. The copolymers of vinylpyrrolidone-trichlorophenylacrylate and vinylpyrrolidone-trichlorophenylmethacrylate were synthesized according to the procedure [7]. The conversion depth is from 10 to 40%. The composition of the copolymers, calculated according to elemental analysis and ultraviolet spectroscopy, for vinylpyrrolidone with trichlorophenylacrylate is 70 molar percent of vinylpyrrolidone and 30 trichlorophenylacrylate, the composition of the VP: THFM copolymer is close to 1: 1.

The diffusion coefficients in dioxane were determined on a diffusometer at a solution concentration of 0.05 g / dl and were taken as diffusion constants. The dependence of the dispersion of the experimental diffusion curves Δ2 on time t, from the slope of which the diffusion coefficients are calculated, is shown in Fig.1.

The refractive index increments were calculated from the areas under the diffusion curves, dn / dc for p-trichlorophenylacrylate in dioxane is (0.09-0.005) cm3 / g. The partial

specific volume is v = 0.55 cm3 / g (dioxane). The molecular weights of the samples of p-trichlorophenylacrylate were calculated using the Swedberg formula using the experimental values of the diffusion and sedimentation constants.

The measurement results of [η], So, D0 and the MSD values for trichlorophenylacrylate are
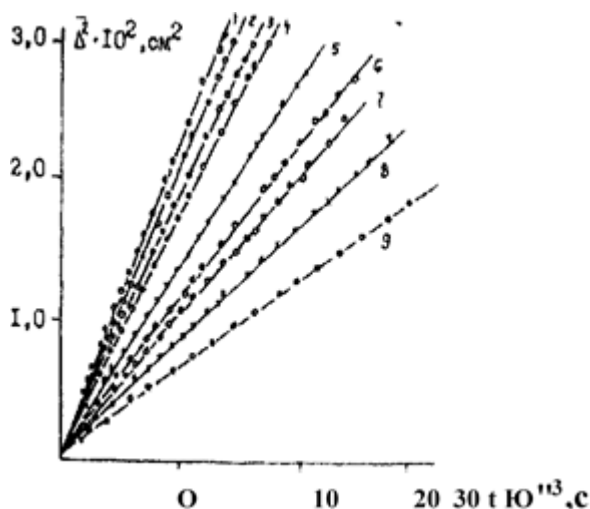

Fig. 1. Dependence of the dispersion of the diffusion curves Δ2 on time t of samples of p-three chlorophenylacrylate in dioxane. Numbers of curves corresponds to numberssamples in table 1.

Table 1.Hydrodynamic characteristics of poly-trichlorophenylacrylate molecules in dioxane:

№ examples	$\eta 10^{-2}$,sm³/g	$D_o 10^7$ sm²/s	S_0 10^{13},s	$M_{SD} 10^{-3}$	$A_o . 10^{10}$,erg/deg	dn/dc, sm³/g
1	0,05	11,4	1,81	11,0	3,60	-
2	0,05	11,0	1,91	12,0	3,35	0,082
3	0,053	9,3	2,07	15,0	2,06	0,096
4	0,055	7,75	2,11	19,0	3,51	0,090
5	0,083	7,4	2,38	22,4	3,6	0,083
6	0,095	5,5	3,92	49,3	3,57	0,089
7	0,11	5,П	4,1	56,0	3,62	0,089
8	0,16	4,2	4,5	74,0	3,82	0,09
9	0,23	3,2	5,6	121,0	3,82	0,09

These dependencies are expressed by the following Mark-Kun-Hauwink equations:

$$S_0 = 1{,}62.10^{-15} M^{0,5}, c$$

given in Table 1. Here are also the hydrodynamic invariant values Ao = ηD (M. [η] / 100) 1/3 T-1 calculated from the experimental values [η] D MSD. In fig. Figure 2 shows, on a double logarithmic scale, the dependences of [η] So and Do on the molecular weight of MSD samples of p-trichlorophenylacrylate.
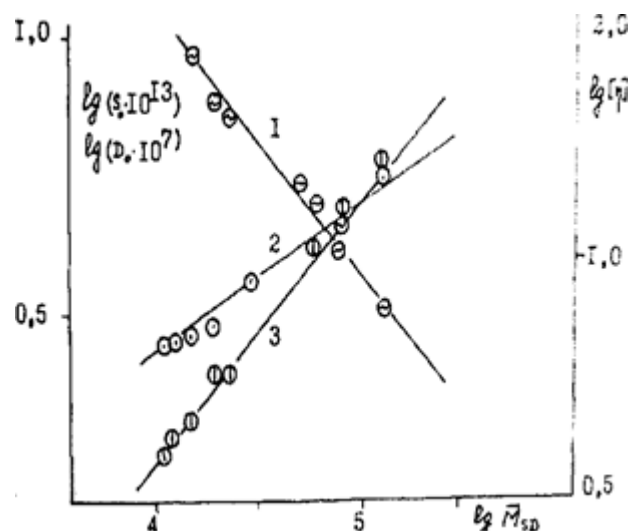

Fig. 2. Logarithmic dependences of D_0 (1), [η] (2), S_o (3) on the M_{SD} samples of p-trichlorophenylacrylate in dioxane.

$$D_0 = l{,}1210^{-4} M^{05}, cm^2/c$$
$$[\eta] = 2{,}95.10^{-2} M^{0,55}, cm^3/г$$

The values of exponents in the equations close to 0.5 indicate the practical absence of volumetric effects in the studied area of molecular masses. Taking this factor into account, the length of the Kuhn statistical segment of p-trichlorophenylacrylate molecules can be calculated from the values of preexponential factors of the equations as in [8].

In this case, for the phenomenon of translational friction, one can use the equations:

$$K_d = (KT / 2\, \eta_o)\, (M_o / A\lambda) = 1.12 \cdot 10^{-4}$$

And for rotational friction:

From $K_\eta \Phi_0 = (A\lambda / M_o)\, 3 / = 2,\ 95.10^{-2}$

The ratio we find the length of the chain segment of p-trichlorophenylacrylate $A_\lambda = 3, 88 \cdot 10^{-8}$ cm with values of P = 5, 11, $\eta_0 = l, 17 \cdot 10^{-3}$, M_o = 251, 5 and $\lambda = 2, 5 \cdot 10^{-8}$ cm. The number of monomer units in the segment $S = Af / \lambda$, = 15.2, from viscometric data $A\eta = 22.10^{-8}$ cm. With a value of the Flory F_o = 2, 86.10^{23} mol^{-1}. When comparing the values of the Kuhn segment lengths found from the translational and rotational friction data, there is a noticeable discrepancy in the values of Af and $A\eta$. The reason for this discrepancy, as was noted in a number of works [8,9], is the use of the theoretical values of the hydrodynamic constants P and Fo in the calculations. The Kuhn segment length for p-trichlorophenylacrylate is 1.5^{-2} times higher than the corresponding value of the flexibility parameter of conventional flexible chain polymers, which may be due to the presence of three chlorine molecules in the side chain of p-trichlorophenylacrylate.

Sedimentation studies of the products of the copolymerization of vinylpyrrolidone with trichlorophenyl (meth) acrylates (synthesized at various initiator contents in the reaction mixture with a conversion depth of 40%). We found the presence in the sedimentograms of two clearly separated peaks (Fig. 3.4), which differ greatly in sedimentation coefficients (table 2).
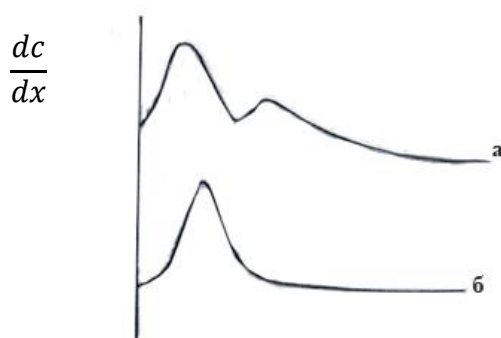

Fig3. Sedimentograms of VP-THFA copolymer (initiator concentration0.025% by weight of copolymers) in dioxane with conversion of k = 40% (a) and k = 17% (b).

Sedimentograms were taken after 45 minutes from the beginning of the acceleration of the rotor.

Figure 4. Sedimentograms of VP-THFA copolymer (initiator concentration0.05% by weight of copolymers) in dioxane at a conversion of 40% (a) and after washing with alcohol (b). Sedimentograms were taken after 62 minutes from the beginning of the rotor acceleration.

An analysis of the data in Table 2 shows that an increase in the initiator content leads to a decrease in the values of sedimentation coefficients of both the first and second peaks. In this case, the difference between S_1 and S_2 of the samples of vinylpyrrolidone-trichlorophenylacrylate copolymer is greater than S_1 and S_2 of vinylpyrrolidone-trichlorophenylmethacrylate.
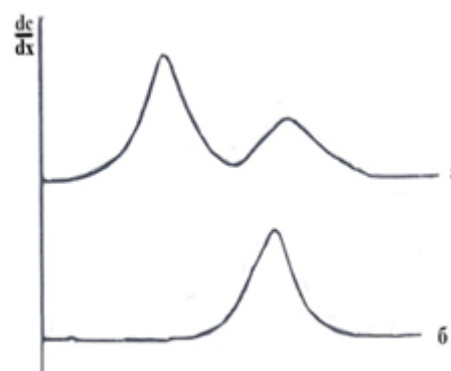
Table 2.Change in the hydrodynamic characteristics of VP-THFA and VP-THFM copolymers depending on the concentration of initiator.

Initiator oncentration	VP-THFA		VP-THFM	
	$S \cdot 10^{13}$,s		$S \cdot 10^{13}$,s	
	1-peak	2- peak	1- peak	2- peak
0,025	7,1	2,5	8,55	2,2
0,05	6,7	2,2	7,9	4,2
0,1	6,6	1,9	7,7	3,8
0,5	6,5	1,5	5,9	3,3
2,0	6,8	2,0	-	-

In order to determine the cause and nature of the resulting copolymerization products, samples of copolymers obtained at low reaction conversions were studied. It was found that during the conversion of 17% for vinylpyrrolidone with trichlorophenylacrylate and 15% for trichlorophenylmethacrylate, the sedimentation of the copolymers is accompanied by the formation of one peak (Fig. 4b).

The copolymers obtained during deep conversions and washed repeatedly with alcohol also give a single peak sedimentogram (Fig. 4b). Therefore, one of the components is removed by dissolving in alcohol. UV spectroscopic studies of washing alcohol solutions reveal the presence of polyvinylpyrrolidone in them.

Thus, the second peak in the sedimentograms of copolymers of vinylpyrrolidone with trichlorophenylacrylate and trichlorophenylmethacrylate with a sedimentation coefficient So is nothing other than polyvinylpyrrolidone.

A study of the kinetic laws of the copolymerization of VP and THFA and the microstructure of the final product revealed an alternation of copolymer units (r_1 = 0.02, r_2 =

0.17) [10]. The studied vinylpyrrolidone-trichlorophenylacrylate copolymer of composition 0.5:0.5 is formed from the initial mixture of copolymers 95: 5 with a conversion of up to 20%. With a deeper conversion, the synthesis of a homopolymer (polyvinylpyrrolidone) begins, which forms the second peak in the sedimentogram.

A similar picture is observed with the copolymerization of vinyl pyrrolidone with trichlorophenylmethacrylate. Comonomertrichlorophenylmethacrylate has a higher reactivity (r_1 = 0.01, r_2 = 1.99). The microstructure of the copolymer of vinylpyrrolidone with trichlorophenylmethacrylate is represented by a block sequence with a predominance of THPM blocks [10]. With a degree of conversion of 16%, trichlorophenylmethacrylate manages completely consumed, with a deepening of the synthesis reaction, a homopolymer (polyvinylpyrrolidone) appears. Therefore, the individuality of the copolymer is determined by the depth of conversion.

Thus, the studies performed allow us to establish the limiting parameters for the conversion of vinyl pyrrolidonecomonomers with trichlorophenyl acrylate (20%) and trichlorophenyl methacrylate (16%) for the final product with a content of reactive monomer units from 30 to 50%.

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