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DETERMINATION OF THE MOLECULAR CHARACTERISTICS OF POLYOLEFINS WITH THE USE OF THE TOMS EFFECT

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The interrelation between the physicochemical properties of macromolecules and the hydrodynamic parameters of a turbulent flow of diluted polymer solutions in a cylindrical channel has been analytically determined. The possibility of estimating of the molecular characteristics of high-molecular polymers with the use of the turborheometric method has been considered. The antiturbulence efficiency of polyhexane used in energy-conserving technologies of pipeline transport of hydrocarbon materials has been analyzed on the basis of comparison of the molecular masses of polymers determined by different methods.

Many polymers can decrease the hydrodynamic resistance of a liquid flow (Toms effect [1]) even in the case where they are present in it in vanishingly small amounts (~1–10 g/m^3). In recent years, this property of polymer solutions has been used for investigating high-molecular compounds [2], in particular, for determining the sizes of macromolecules and their molecular masses [3, 4]. In order that the properties and parameters of individual macromolecules could be investigated, it is necessary that these macromolecules be separated by distances at which the intermolecular interactions between them are negligibly small.

Since polymer molecules are not transformed into the gas state, the above-indicated condition can be realized in very dilute solutions, in which these molecules roll up statistically into noncontiguous balls with an immobilized (embedded) solvent. To rationally use macromolecules in energy-conserving technologies, e.g., in the pipeline transport of liquids, it is necessary to know their properties and structure.

The empirical attempts to estimate the molecular characteristics of polymers by their influence on the rate of a turbulent flow were made by researchers beginning with the instant the Toms effect was discovered. However, the estimations made were, as a rule, qualitative in character because of the absence of analytical relations between the physicochemical properties of macromolecules and the hydrodynamic parameters of a flow. This problem can be solved numerically on the basis of an equation proposed by us in [5] for the dependence of the increment of the volumetric rate of a polymer-solution flow $\Delta Q = Q_p - Q_s$ in a cylindrical channel on the shear stress on its wall τ and the volume fraction Ψ of macromolecular balls with a modulus of elasticity G:

$$\Delta Q = S\tau\Psi\,[1 - (G/\tau)^{1/2}]/(\rho G)^{1/2}\,. \tag{1}$$

The quantities Ψ and G, representing rheological characteristics of the Toms effect, depend on the concentration, sizes, and chemical nature of macromolecules forming, in a solution, balls with an immobilized solvent. The sizes of these balls are mainly determined by the molecular mass M of a polymer and the degree of its chemical affinity for a solvent (characteristic viscosity $[\eta]$).

The volume of a spherical ball can be calculated using the Flory–Fox formula $(h^2)^{3/2} = [\eta]M/\Phi$ and the known relation of statistical physics of polymers $r^2 = h^2/6$, relating the hydraulic radius of a macromolecule to the root-mean-square distance between the ends of its chain:

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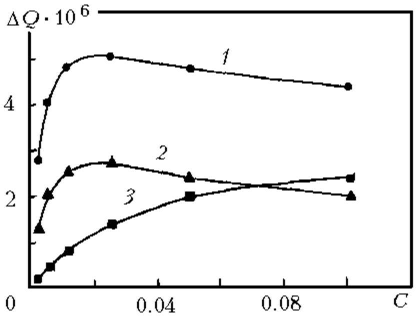

Fig. 1. Dependence of the increment of the volumetric rate of flow on the concentration of polyhexane in benzene: 1) τ = 11 Pa, $[\eta]$ = 1.71 m^3/kg, V_b = $20.8 \cdot 10^{-21}$ m^3; M_h = 9120 kg/mole; 2) τ = 4 Pa, $[\eta]$ = 1.71 m^3/kg, V_b = $20.8 \cdot 10^{-21}$ m^3, M_h = 9120 kg/mole; 3) τ = 11 Pa, $[\eta]$ = 0.48 m^3/kg, V_b = $2.8 \cdot 10^{-21}$ m^3, M_h = 4370 kg/mole. C, kg/m^3; ΔQ, m^3/sec.

$$V_b = 0.28M\,[\eta]/\Phi\,. \tag{2}$$

For the Flory constant $\Phi = 2.1 \cdot 10^{23}$ mole^{-1} [6], the numerical coefficient is approximately equal to the Avogadro number $\Phi/0.28 \approx N_A$; in this case,

$$V_b = \frac{M\,[\eta]}{N_A}\,. \tag{3}$$

A polymer ball is predominantly filled (impregnated) with particles of a low-molecular solvent such that each elementary main-chain link is surrounded by several hundred solvent molecules comparable to it in size; this being so, the density of the macromolecular balls ρ_b and the solvent density ρ_s are approximately equal ($\rho_b \approx \rho_s$). The equality of these densities results in the polymer "drops" executing Brownian motion being distributed uniformly in the solvent volume. The elementary main-chain links and solvent particles solvating them are connected by the intermolecular-interaction forces; because of this, the polymer chain serves as the reinforcing fragment of the medium. Therefore, we suggest that a polymer addition prevents turbulence rather than suppresses it.

Since macromolecules with an immobilized solvent have much larger sizes than the corresponding closely rolled-up globules, which have the same molecular mass but do not have emptinesses for solvent molecules, the properties of a diluted polymer solution are determined by the volume fraction $\Psi = \Sigma V_b/V$ of the molecules noncontacting with the embedded solvent in this solution rather than the polymer concentration C.

If N polymer balls with equal volumes of macromolecules V_b are contained in a diluted solution ($V_s >> NV_b$) with a total volume $V = V_s + \Sigma V_b$, $\Psi = NV_b/(V_s + NV_b) = (NV_b/V_s)/(1 + NV_b/V_s)$, where V_s is the total volume of nonimmobilized solvent molecules located beyond the sphere of balls. These equations can be simplified using expression (2) and formulas for calculating the molar mass $M = N_A \mu$ ($N_A = 6.02 \cdot 10^{23}$ mole^{-1}). Then, for ultimately dilute solutions ($S_s >> NV_b$), we obtain

$$\Psi = \frac{[\eta]\,C}{1 + [\eta]\,C}\,. \tag{4}$$

As follows from Eq. (4), the dependence of the volume fraction of macromolecular balls in a solution on the concentration of a polymer represents a saturating curve that tends asymptotically to unity when the polymer content increases. The slope of the initial portion of curve (4) is determined by the characteristic viscosity or, in accordance with the Mark–Kuhn–Hauwink equation $[\eta] = K(\text{MM})^{\alpha}$ (K, α are empirical coefficients), by the molecular mass of the polymer. Therefore, the increment of the volumetric rate of flow in ultimately dilute solutions ($[\eta]C << 1$) increases with increase in the molecular mass (Fig. 1).

An individual macromolecule with an immobilized solvent can also be considered as a "microphase," i.e., as a solvent volume structured by an arbitrary rolled chain and possessing viscous and elastic properties differing from the properties of the environment.

Extending the known formula [7] used in rheology for calculating the elasticity of polymer solutions $G = CRT/M$ to a macromolecular ball and taking into account the fact that the concentration of a polymer in a ball with an immobilized solvent is determined by the ratio between the mass of the polymer chain $\mu = M/N_A$ and the volume of the "drop" $C = \mu/V_b$, we obtain a formula for calculating the modulus of elasticity of an individual ball:

$$G = kT/V_b\,. \tag{5}$$

Substituting (5) into Eq. (1) gives

$$\Delta Q = S\tau\Psi\,(V_b/\rho kT)^{1/2}\,[1-(kT/\tau V_b)^{1/2}]\,. \tag{6}$$

From (6) follows the initial (threshold) condition for the appearance of the Toms effect, at which the volumetric rate of a polymer-solution flow is larger than the rate of a solvent turbulent flow, i.e., the condition $\Delta Q > 0$ is possible when $\tau V_b > kT$. Using formula (3), we obtain the following relation from this inequality:

$$\tau\,[\eta]\,M > RT\,, \tag{7}$$

from which it is obvious that the larger the molar mass of a polymer and the better its compatibility with a solvent, i.e., the larger $[\eta]$, the smaller the "threshold" shear stress $\tau_{thr} = RT/(M[\eta])$.

Under the conditions of a developed turbulent flow, which are realized at fairly large shear stresses, the value of $kT/(\tau V_b)$ tends to zero and Eq. (6) becomes simpler:

$$\Delta Q = S\tau\Psi\,(V_b/\rho T)^{1/2}\,. \tag{8}$$

Expression (8) is adequate to the available empirical data on the Toms effect (Fig. 1) and allows one to determine the volumes of macromolecular balls in the process of turborheometric investigations.

The volumetric rates of flows of polymer solutions Q_p and solvents Q_s were measured on a turborheometer [2], which is similar in design to a capillary viscosimeter but allows one to carry out measurements in a fairly wide range of shear stresses characteristic of both the laminar and turbulent regions of a flow. Methods of calculating the volume of balls in the region of small concentrations, which do not exceed the "optimum" concentration, are described in detail in [3, 4]. The optimum concentration C_{opt} is a concentration at which ($\Psi = 1$) balls with an immobilized solvent begin to come in contact with each other; further increase in the concentration of balls leads to their mutual deformation, i.e., compression (decrease in V_b) and, in accordance with Eq. (8), to a slow decrease in the increment of the volumetric rate of flow ΔQ (see Fig. 1). The quantities V_b and $[\eta]$ are experimentally determined by the hydrodynamic (turborheometric and viscosimetric) methods, and the molar mass of a polymer sample M_h is calculated by formula (2).

It follows from expressions (6)–(8) that the sizes of the macromolecular balls significantly influence both the onset of the Toms effect and its value. Therefore, in pipelines for transport of petroleum, it is necessary to use polymers that are well dissolved in hydrocarbon liquids ($[\eta] > 1$ m^3/kg) and have a large molar mass ($M > 1\cdot 10^3$ kg/m^3), at which relation (7) is fulfilled at a shear stress of several pascals at the wall of a pipe.

At the present time, poly-α-olefins are most frequently used for these purposes. The polyhexane samples synthesized by us were dissolved in benzene and then tested by the viscosimetric and turborheometric methods for the purpose of determining the value of $[\eta]$, V_b, and M_h; they were also investigated by the method of vacancy permeation chromatography (see Table 1).

The molar-mass distribution of polyhexane samples in 1,2,4-trichlorobenzene at a temperature of 140°C was measured on a Waters-150C gel chromatograph complete with a differential viscosimeter. Separation was performed in four TSK-GEL columns (Tosoh Corp.) that were connected successively. Calibration was carried out with the use of narrow polystyrene standards with a molecular mass of 10^3–10^7. The molecular-mass distribution was calculated by the universal calibration $M[\eta]$ depending on the retained volume.

TABLE 1. Characteristic Viscosity, Volume of Balls, and Molar Mass of Different Polyhexane Samples

Sample	$[\eta]$, m^3/kg	$V_b \cdot 10^{21}$, m^3	M_h, kg/mole	M_w, kg/mole	M_n, kg/mole	M_w/M_n
1	1.71	20.8	9120	9600	1500	6.4
2	1.25	14.6	8760	8700	1600	5.4
3	1.24	14.0	8470	9000	1300	6.9
4	0.48	2.8	4370	5300	680	7.8

Note. The values of $[\eta]$, V_b, and M_h were determined by hydrodynamic methods, and the values of M_w and M_n were determined by the method of vacancy permeation chromatography.

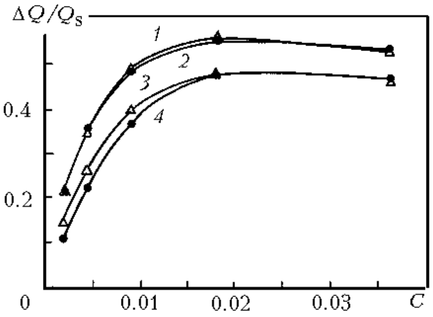

Fig. 2. Dependence of the antiturbulence efficiency of samples 2 (1, 3) and 3 (2, 4) (see Table 1) of polyhexane in benzene on their concentration: 1, 2) $\tau = 11$ Pa; 3, 4) $\tau = 4$ Pa. C, kg/m^3.

As follows from Table 1, the molar masses of the first three polyhexane samples M_h, determined by the hydrodynamic methods (viscosimetric and turborheometric), are in satisfactory agreement with the weight-average molar masses M_w of these samples determined by the method of vacancy permeation chromatography. The somewhat larger difference (~20%) between M_h and M_w of the fourth sample is explained by the fact that the smaller the volume of a polymer ball at a given shear stress, the larger the value by which the algebraic sum in square brackets differs from unity. Because of this, when the simplified equation (8) is used instead of (6) for calculating V_b after turborheometric measurements, the volumes of macromolecules and their molecular masses become somewhat underestimated.

A specific feature of the synthesis of polyolefins with the use of Ziegler–Natta catalysts is the formation of polydisperse products with a fairly large molecular-mass distribution characterized by the ratio between the weight-average molecular mass and the number-average mass M_w/M_n. Comparison of the antiturbulence efficiency ($\Delta Q/Q_s$) of two polyhexane samples (sample 2 and sample 3, see Table 1), having close values of $[\eta]$ and M_h but different polydispersities, has shown (Fig. 2) that their antiturbulence efficiencies are practically equal at large shear stresses ($\tau = 11$ Pa) and are somewhat different at small shear stresses ($\tau = 4$ Pa). This is explained evidently by the fact that, at small shear stresses, a large part of the macromolecules having low molecular masses do not satisfy condition (7) and do not serve to decrease the resistance, i.e., represent a "ballast." In sample 3 with a smaller value of M_n and a larger value of molecular-mass distribution, the fraction of such nonactive macromolecules is larger; therefore, a relative increase in the volumetric flow rate $\Delta Q/Q_s$ (the value of the effect) will decrease with decrease in the shear stress.

Thus, experimental data on the molecular characteristics of polymers (V_b and M_h) allow one to predict the possibility of using them in energy-conserving technologies of pipeline transport of hydrocarbon liquids. For example, testing of polyhexane samples 1–3 on a turbulent rheometer has shown that they substantially decrease the hydrodynamic resistance of a turbulent liquid flow ($C_{opt} \approx 20$ g/m^3) and therefore can be recommended for use in the process of transport of petroleum and petroleum products. The "threshold" shear stresses of these polymers ($\tau_{thr} = 0.1$–0.2 Pa) are much lower than the actual shear loads in main-road pipelines (1–10 Pa), which guarantees the obtaining of a technological effect in the case of their use. A much larger amount of the low-molecular sample 4 is required per unit volume of a transported liquid ($C_{opt} > 100$ g/m^3) to increase the rate of a turbulent flow; this polymer can be recommended only for pipelines in which flows have a shear stress $\tau > 2$ Pa on the wall.

NOTATION

C, concentration of a diluted polymer solution, kg/m^3; *G*, modulus of elasticity of macromolecular balls, Pa; *k*, Boltzmann constant, J/K; *M*, molar mass of a polymer, kg/mole; MM, relative molecular mass of a polymer; M_n, number-average molecular mass; M_w, weight-average molecular mass; N_A, Avogadro number, mole^{-1}; *R*, universal gas constant, J/(mole·K); *Q*, volumetric rate of flow, m^3/sec; *S*, area of the cross section of a pipe, m^2; *T*, absolute temperature, K; *V*, volume of a macromolecule ball, m^3; [η], characteristic viscosity of a polymer solution, m^3/kg; μ, physical mass of the polymer chain, kg; ρ, density of a liquid, kg/m^3; τ, shear stress, Pa; Φ, Flory constant, mole^{-1}; Ψ, volume fraction of polymer balls in a solution. Subscripts: w, weight; n, number; p, polymer solution; s, pure solvent; h, hydrodynamic; thr, threshold; opt, optimum; b, ball.

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